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ON SALTS OF NITROPARAFFINS, AND ACYLATED DERIVATIVES OF HYDROXYLAMINE.

By Lauder W. Jones.

Of all the properties shown by the primary and secondary nitroparaffins, the two which seem to be the most characteristic are their tendency to form salts, and the peculiar power which they possess in the iso-form, either as salts or as esters, of producing oxidation-reactions. We are indebted chiefly to Nef[1] for our present conception of the salts. It was shown by him, that different constitutional formulæ must be assigned to the true nitro bodies and to their salts and esters, and that the metal or radical is bound to oxygen

$$\left(\begin{array}{c} R{-}CH{=}N{-}O{-}M \\ \| \\ O \end{array} \right)$$ and not to carbon ; the discovery of iso-

phenylnitromethane by Hantzsch and Schultze[2] confirms the work of Nef.

It was stated in the paper on the nitroparaffins, that the action of acid chlorides on the salts would be studied ; that experiments with the yellow mercury salt obtained by the action of mercuric chloride on sodium isonitromethane, and attempts to synthesize esters of carbon dioxide oxime, $R{-}O{-}N{=}C{=}O$, would be continued. During the last

[1] Ann. Chem. (Liebig), 280, 263.   [2] Ber. d. chem. Ges., 29, 699, 2251.

three years, I have carried out further investigations along these lines under the direction of Dr. Nef, and now present my results in detail.[1]

I. THE ACTION OF ACID CHLORIDES ON SODIUM ISONITRO-ETHANE AND SODIUM ISONITROMETHANE.

1. _The Action of Benzoyl Chloride on Sodium Isonitroethane._

The sodium isonitroethane used in the following experiments was prepared by adding sodium ethylate to an alcoholic solution of nitroethane. After filtering the salt, and washing thoroughly with alcohol and ether, it was carefully dried in a vacuum-desiccator to remove every trace of alcohol.

It was expected that the first product formed by the action of benzoyl chloride on sodium isonitroethane would be benzoylisonitroethane,

$$CH_3—CH=N—O—Na + C_6H_5—COCl =$$
$$\overset{\|}{\underset{O}{}}$$

$$CH_3—CH=N—O—CO—C_6H_5 + NaCl.$$
$$\overset{\|}{\underset{O}{}}$$
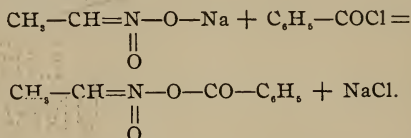
The reaction, however, is more complex in its nature, and benzoylisonitroethane undergoes a peculiar intramolecular oxidation, giving rise to an isomeric substance, the benzoyl ester of acethydroxamic acid.

$$CH_3—CH=N—O—CO.C_6H_5 \rightarrow CH_3—C\begin{cases} O—H \\ N—O—COC_6H_5 \end{cases}$$
$$\overset{\|}{\underset{O}{}}$$
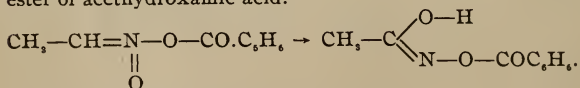
This rearrangement furnishes a basis for the interpretation of the reaction. The benzoyl ester of acethydroxamic acid is a stronger acid than isonitroethane and decomposes sodium isonitroethane, setting free nitroethane, and forming the sodium salt of the benzoyl ester of the acethydroxamic acid,
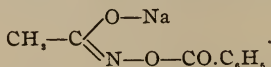
$$CH_3—C\begin{cases} O—Na \\ N—O—CO.C_6H_5 \end{cases}$$

In the presence of benzoyl chloride, this salt is converted into triacylated hydroxylamine derivatives, neutral substances, which constitute the chief products of the reaction.

Essentially the same results are obtained, with slight variations in the relative amounts of acid and neutral products, whether the reacting substances are dissolved in water or suspended in absolute ether. In each of the following experiments 20 grams of sodium salt were dissolved in 100 grams of water, and 28.8 grams of benzoyl chloride added; the table shows the relative quantities of acid and neutral products.

Experiment.	Soluble in NaHCO₃. Grams.	Soluble in NaOH. Grams.	Neutral Oil. Grams.
I.	6.5	3.2	12.3
II.	..	7.2	18.0
III.	6.5	7.0	16.5

Two experiments were performed, the substances being suspended in absolute ether: In Experiment I., 20 grams of sodium salt were suspended in 135 grams of absolute ether, and 28.8 grams of benzoyl chloride added; in Experiment II., 17.8 grams of sodium salt, 120 grams of absolute ether, and 25.0 grams of benzoyl chloride were used.

Experiment.	Soluble in NaHCO₃. Grams.	Soluble in NaOH. Grams.	Neutral. Grams.	Solid residue. Grams.
I.	4.7	3.5	19.3	13.5
II.	3.3	2.6	17.5	12.0

These two experiments were more favorable for a detailed study of the reaction than those carried out in water solution; they have been chosen as representative, and will be described in the account which follows.

17.5 grams of finely powdered sodium salt were suspended in 120 grams of absolute ether; the flask containing the mixture was placed in ice-water, and 25 grams (1 mol. = 25.7 grams) of benzoyl chloride were added in small portions. After standing a few minutes, the ether assumed a greenish hue, which finally passed into orange. The mixture was kept at 0° for two hours, and then allowed to stand at the temperature of the room, until the odor of benzoyl chloride was no longer noticeable.

The insoluble residue, removed by filtration, weighed 12

grams, and was composed chiefly of sodium chloride, with a
small amount of sodium nitrite ; no unchanged sodium iso-
nitroethane was present.

The ether filtrate was placed in a distilling-bulb and sub-
jected to distillation at reduced pressure ; the distillate passed
through a long, well-cooled condenser, and was caught in a
receiver surrounded by a freezing-mixture. When most of
the ether had passed off, the pressure was diminished to 130
mm., and the temperature of the water-bath increased to 75°;
at 85°, the thick, yellow oil in the distilling-bulb began to turn
red, and to prevent further decomposition, the distillation was
interrupted. The small amount of colorless liquid, which
accumulated in the receiver, gave, on redistilling, 2 grams
of nitroethane, boiling at 113°–114°, which was identified by
its properties, and by converting it into ethylnitrolic acid.

The oil remaining in the distilling-bulb, which still pos-
sessed a strong odor of nitroethane, was redissolved in ether,
and the ether solution extracted, first with sodium bicarbonate
(A), and then with dilute sodium hydroxide (B) (containing
10 grams of the hydroxide in 100 grams of water). The ether
containing the neutral portion (C) was washed carefully with
water, dried with calcium chloride, and the ether then allowed
to evaporate in a vacuum-desiccator.

A. *Portion Soluble in Sodium Bicarbonate.*

Benzoyl ester of acethydroxamic acid, $CH_3—C \underset{N—O—COC_6H_5}{\overset{O}{\diagup\diagdown}}$
$\underset{H}{|}$
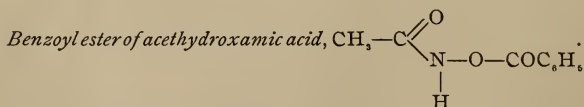
—After acidifying the bicarbonate solution with dilute sul-
phuric acid, it was extracted with ether ; 3.3 grams of crystal-
line material were obtained on evaporating the ether, which
proved to be a mixture of two substances, benzoic acid, and
the benzoyl ester of *acethydroxamic acid*.

A separation of these two substances was easily effected by
treatment with boiling ligroïn (40°–60°), which readily dis-
solves benzoic acid. By this method the solid (3.3 grams) was
separated into 2 grams of benzoic acid (melting-point 119°–

120°), and 1.3 grams of the benzoyl ester of acethydroxamic acid.

The latter exists in two forms: A part, 6.8 grams, was obtained by crystallizing from ether in large, well-developed crystals, melting at 98°–99°. The second form is more soluble in ether, and can be precipitated from ether, after the other form has crystallized out, by means of low-boiling ligroïn, in flat, transparent crystals, melting at 69°–70°. After standing for several days, this form becomes opaque, and in the course of a week or two passes completely into the high-melting form.[1] It is possible that this low-melting form is a hydroximic acid,

$$CH_3-C\begin{cases} O-H \\ N-O-CO.C_6H_5 \end{cases}$$, and that the change, which it

undergoes on standing, is due to a rearrangement to form a

hydroxamic acid, $CH_3-C\begin{cases} O \\ NHOCO.C_6H_5 \end{cases}$.

0.1257 gram, melting at 98°–99°, gave 0.2793 gram CO_2, and 0.0593 gram H_2O.

0.1282 gram gave 9 cc. N_2 at 14° and 749 mm.

	Theory for $C_9H_9NO_3$.	Found.
C	60.33	60.27
H	5.02	5.15
N	7.83	8.16

Properties of the Benzoyl Ester of Acethydroxamic Acid.—It is readily soluble in alcohol, less soluble in chloroform, or ether, sparingly soluble in cold water, and almost insoluble in ligroïn, and benzol.

Towards alkalies it is quite sensitive, and is readily decomposed by them into benzoic acid and acethydroxamic acid,

$CH_3-C\begin{cases} O \\ N-HOH \end{cases}$. Even boiling water causes the same

decomposition, but much less readily. On heating, it is completely decomposed; benzoic acid, methyl isocyanate, and a brown residue are formed.

[1] By adding acid to a water solution of the sodium salt of the form melting at 98°–99°. and extracting with ether, a mixture of the two forms is obtained.

Sodium Salt, $CH_3-C\begin{smallmatrix}O-Na\\N-O-CO.C_6H_5\end{smallmatrix}$.—By adding sodium ethylate to an alcoholic solution of the acid, and precipitating with absolute ether, a white, crystalline salt was obtained.

0.2582 gram gave 0.0843 gram Na_2SO_4.

	Theory for $C_9H_8NO_3Na$.	Found.
Na	11.43	11.46

This salt is readily soluble in water, and from this solution a white, non-crystalline silver salt can be precipitated by silver nitrate.

Synthesis of the Benzoyl Ester of Acethydroxamic Acid from Acethydroxamic Acid.—In order to establish the identity of the substance obtained from nitroethane, with the benzoyl ester of acethydroxamic acid, it was necessary to prepare this compound synthetically. 4 grams of acethydroxamic acid, $CH_3-C\begin{smallmatrix}O\\NHOH\end{smallmatrix}$, (melting-point 88°–89°), prepared according to the method described by Miolati[1], were dissolved in 50 grams of water, and neutralized with 3 grams of potassium hydroxide in 25 grams of water. To this solution, well cooled, 7.5 grams of benzoyl chloride were added in small portions, shaking thoroughly after the addition of each portion. In a few minutes a dense, crystalline mass accumulated. This was collected on a filter, and pressed on a clay plate to remove water, and some unchanged benzoyl chloride. The dry product was treated with boiling ligroïn, which took up a small amount of benzoic acid.

This crude product (6.5 grams) was dissolved in ether. On standing, large, transparent crystals, melting at 98°–99°, were formed, which were identical in every respect with the substance obtained from nitroethane.

0.1796 gram, melting 98°–99°, gave 0.3975 gram CO_2, and 0.0842 gram H_2O.

0.2423 gram gave 16.9 cc. N_2 at 18° and 742.7 mm.

[1] Ber. d. chem. Ges., **25**, 700.

	Theory for $CH_3-C\overset{O}{\underset{NHOCO.C_6H_5}{}}$	Found.
C	60.33	60.36
H	5.02	5.20
N	7.83	7.90

In this case, also, two forms were observed. Of the 6.5 grams, 4.6 grams melted at 98°–99°, while 1.8 grams separated in flat crystals, melting at 69°–70°.

The absolute identity of the substance obtained from nitroethane (melting-point 98–99°), with the benzoyl ester of acethydroxamic acid, is established by the identity of the crystalline forms.

For the following crystallographic data, I am indebted to Mr. Zirngiebl, who kindly carried out the measurements of these two substances in Prof. Groth's laboratory at Munich.

Crystal system : monoclinic.
a : b : c = 1.4623 : 1 : 1.4545
$\beta = 94° 41'$

The forms which were observed are : 001, 110, 101, 11$\bar{1}$, 100 ; the last two are sometimes wanting.

001 : 100 = 85° 19'
001 : 101 = 42° 31'
110 : $\bar{1}$10 = 68° 43'

Cleavage completely in 001.
The plane of the optical axes ⊥ 010.

B. Portion Soluble in Sodium Hydroxide.

The solution in sodium hydroxide possessed an intense red color, which disappeared on acidifying with dilute sulphuric acid, and was due, as will be shown, to the presence of salts of ethylnitrolic acid. By means of ether 2.6 grams of crystalline material were extracted. This solid proved to be a mixture of the following substances :

	Grams.
Benzoic acid,	1.9
Benzoyl ester of benzhydroxamic acid,	
$C_6H_5-C\overset{O}{\underset{NHO.CO.C_6H_5}{}}$,	0.4

Benzoyl ester of acethydroxamic acid,

$$CH_3—C\underset{NHOCO.C_6H_5}{\overset{O}{<}},$$ traces.

Ethylnitrolic acid $CH_3—C\underset{N—O—H}{\overset{NO_2}{<}}$, traces.
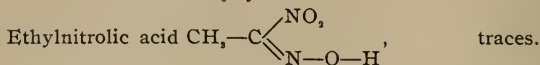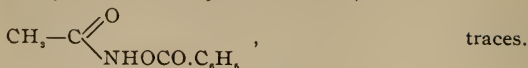
A separation of these substances was accomplished as follows: The entire residue (2.6 grams) was dissolved in the smallest possible amount of sodium hydroxide, and carbon dioxide conducted into the solution until no more benzoyl ester of benzhydroxamic acid (dibenzhydroxamic acid) separated. This substance was removed by filtration, and extraction with ether. Recrystallized from alcohol, it separated in fine needles, melting at 158°–159°. A portion was converted into the potassium salt, and this, by boiling with water, into diphenylurea (melting at 235°–236°).

A nitrogen determination was also carried out.

0.2968 gram gave 15.1 cc. N, at 16.5° and 756.8 mm.

	Theory for $C_{14}N_{11}NO_3$.	Found.
N	5.80	5.90

The filtrate was acidified, and the benzoic acid which separated, collected on a filter and dried. It melted at 117°–118°, and contained traces of the benzoyl ester of acethydroxamic acid.

The acidified solution, from which the benzoic acid had been removed, was neutralized with sodium hydroxide; to the deep-red solution a few drops of benzoyl chloride were added, and the mixture shaken until a yellow crystalline solid deposited. After recrystallizing from boiling alcohol, this solid melted at 134°–135°, and was identical with the benzoyl ester of ethylnitrolic acid, $CH_3—C\underset{N—O—CO.C_6H_5}{\overset{NO_2}{<}}$, which melts at 135°. 0.4 gram was obtained.

These substances are undoubtedly formed by the decomposition of the neutral portion in the presence of sodium hydroxide. The formation of ethylnitrolic acid is explained by the presence of the benzoyl ester of ethylnitrolic acid,

$$CH_3—C\begin{matrix} \diagup NO_2 \\ \diagdown NOCOC_6H_5 \end{matrix}$$. When benzoyl chloride acts on so-
dium isonitroethane in water solution, larger amounts of this
benzoyl compound are formed, and crystallize from the neu-
tral oil on standing. Its presence is to be explained by a decom-
position of sodium isonitroethane, with formation of nitrous
acid; the green color, which the ether solution first assumes,
points to this decomposition. Nitrous acid reacts with
sodium isonitroethane to form ethylnitrolic acid, which is a
stronger acid than isonitroethane, and decomposes sodium iso-
nitroethane, forming the sodium salt of ethylnitrolic acid.
This reacts with benzoyl chloride to form the benzoyl ester of
ethylnitrolic acid. The formation of dibenzhydroxamic acid,
$C_6H_5CO.NHOCOC_6H_5$, and the benzoyl ester of acethydrox-
amic acid will be explained, when the nature of the neutral
portion is discussed.

C. Neutral Portion.[1]

Benzoyl Ester of Benzoylacethydroxamic Acid,

$$CH_3—C\begin{matrix} \diagup O—COC_6H_5 \\ \diagdown NOCOC_6H_5 \end{matrix}$$, and *α-Benzoyl-β-acetylbenzoylhydrox-*

ylamine, $\begin{matrix} CH_3—CO \\ C_6H_5—CO \end{matrix} \diagdown\diagup N.O—CO—C_6H_5.$
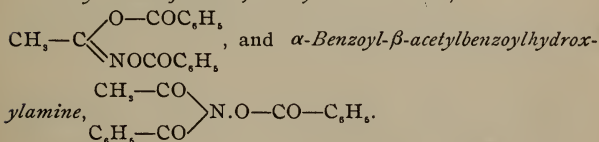
After the ether and volatile portions had passed off, 17.5
grams of thick, reddish oil remained. When the amount of
material taken is compared with the amount recovered, it be-
comes apparent that considerable loss has occurred.

	Taken. Grams.		Found. Grams.
Sodium isonitroethane,	17.8	Neutral,	17.5
Benzoyl chloride,	25.0	Acid,	5.9
	———	Solid residue,	12.0
	42.8	Nitroethane,	2.0
Loss = 5.4 grams.			37.4

[1] The neutral oil is not, as was at first supposed, a mixture containing "Tribenz-
hydroxylamine," $C_6H_5C\begin{matrix} \diagup OCOC_6H_5 \\ \diagdown NOCOC_6H_5 \end{matrix}$, as one of its ingredients, but a mixture of the
two isomers given above. *Vide* Ber. d. chem. Ges., **29**, 1218.

As no evolution of gas occurred, this loss must have been due to volatile liquid, and in view of the fact that nitroethane was recovered, and that the oil still possessed a strong odor of nitroethane, almost the entire loss must be attributed to regenerated nitroethane, except perhaps slight losses which occurred in extracting with sodium bicarbonate and sodium hydroxide.

The regenerated nitroethane would, on this basis, amount in all to 7.4 grams (5.4 grams + 2.0 grams), which is a little more than half of the nitroethane used.

7.4 grams of nitroethane = 9.5 grams of sodium isonitroethane.

One-half of the sodium salt used, 17.8 = 8.9 grams.

Properties of the Oil.—This oil showed no signs of solidifying in a freezing-mixture, and even after an exposure of several weeks to the extremest cold of winter weather, only a slight deposit was formed, and this redissolved on attempting to separate it from the oil.

It cannot be distilled, even under diminished pressure, without undergoing complete decomposition, with the formation of benzoic acid, acetic acid, an isocyanate, and a brown, non-volatile residue.

On warming a few drops of the oil with dilute alkali, it is decomposed ; dilute sulphuric acid precipitates benzoic acid, and the acidified solution gives an intense reaction with ferric chloride, indicating the presence of hydroxamic acids.

The behavior of the oil towards concentrated hydrochloric acid, its behavior towards alcoholic potash, and an analysis show that it is a triacylated hydroxylamine derivative, to which the empirical formula, $(CH_3CO)(C_6H_5CO)_2ON$, must be assigned.

Behavior towards concentrated Hydrochloric Acid.—The oil is decomposed by concentrated hydrochloric acid into benzoic acid, acetic acid, and hydroxylamine hydrochloride, with traces of ammonium chloride.

5.0 grams were heated with 2–3 volumes of acid for two hours at 100° in a sealed tube. No pressure was observed on opening the tube.

The benzoic acid was filtered, washed once with ice-water, dried, and weighed. It was found to weigh 4.1 grams, while 4.3 grams is the amount calculated for $(CH_3CO)(C_6H_5CO)_2ON$.

The filtrate was diluted with water to a volume of 250 cc., and distilled until two-thirds of this volume had passed into the receiver. This distillate was treated with silver carbonate, heated to boiling, filtered, and evaporated to dryness on a water-bath. In this way 1.0 gram of silver acetate was obtained, which, after recrystallizing from hot water, and washing with absolute alcohol to remove traces of silver benzoate, gave the following figures on analysis:

0.1120 gram gave 0.0722 gram Ag.

	Theory for CH_3—$COOAg$.	Found.
Ag	64.66	64.46

The hydrochloric acid solution, which remained in the distilling-bulb, was evaporated to dryness in an evaporating-dish over a water-bath; 0.8 gram of the solid residue remained, consisting chiefly of hydroxylamine hydrochloride, with traces of ammonium chloride. It reduced Fehling's solution, and was converted into acetoxime; volatile, prismatic crystals were obtained, melting at 59°–60°.

Analysis.—The neutral oil, carefully washed with sodium bicarbonate and sodium hydroxide, and freed from volatile substances by standing *in vacuo* for two weeks, gave the following figures on analysis:

0.1658 gram gave 0.4175 gram CO_2, and 0.0690 gram H_2O.
0.1307 gram gave 0.3282 gram CO_2, and 0.0575 gram H_2O.
0.3407 gram gave 13 cc. N_2 at 21° and 748 mm.

	Theory for $(CH_3CO)(C_6H_5CO)_2ON$.	I.	Found. II.	III.
C	67.84	68.66	68.48	....
H	4.62	4.62	4.88	....
N	4.92	....	....	4.29

Considering the nature of the oil, and its method of preparation, the figures obtained agree well with the theory.

Behavior of the Oil towards Alcoholic Potash.

6.2 grams were dissolved in a few cubic centimeters of alco-

hol, and, after cooling the solution, 2.3 grams of potassium hydroxide (calculated 2 mol. = 2.4 grams), dissolved in a few grams of alcohol, were added.   Almost immediately a crystalline salt formed, which increased on standing ; after five minutes this salt was filtered from the deep-red alcoholic solution.   It weighed 3.7 grams, and was composed of the potassium salts of benzoic acid and of the benzoyl ester of benz-

$$\text{hydroxamic acid,}\ C_6H_5\text{---}C\underset{\textstyle NOCOC_6H_5}{\overset{\textstyle OK}{<}}.$$

A separation of these two acids was accomplished by dissolving the mixture of the salts in water, and passing carbon dioxide through the solution.   Thus 1.0 gram of the benzoyl ester of benzhydroxamic acid, melting at 158°–159°, was precipitated. It was also identified by converting it into diphenyl urea.   On acidifying the filtrate, and extracting with ether, 1.6 grams of benzoic acid (melting-point 119°–120°) were obtained.

The original alcoholic solution was diluted with water and extracted with ether.   2.7 grams of the ethyl benzoate, boiling at 209°–212°, were obtained on distilling.

The solution was then acidified with dilute sulphuric acid, and extracted with ether.   A solid, crystalline residue remained on evaporating the ether, which, recrystallized from ether and low-boiling ligroïn, gave 0.1 gram of the benzoyl ester of acethydroxamic acid, melting at 98°–99°, and 0.4 gram, melting at 69°–70°.

The presence of hydroxamic acids could be shown in the remaining solution by means of ferric chloride.

The results may be summed up as follows:

6.2 grams of oil gave :

	Grams.
Benzoyl ester of benzhydroxamic acid,	1.0
Benzoyl ester of acethydroxamic acid,	1.4
Benzoic acid,	1.6
Ethyl benzoate,	2.7

The formation of the benzoyl ester of acethydroxamic acid, $CH_3\text{---}CO.NH.CO.C_6H_5$, and benzoic acid (partially as ethyl

benzoate), can only be explained by the presence of the benzoyl ester of benzoylacethydroximic acid, $CH_3-C\begin{cases} O.CO.C_6H_6 \\ NO.CO.C_6H_5 \end{cases}$, in the neutral oil. If the oil were made up entirely of this substance, it is impossible to account for the formation of the benzoyl ester of benzhydroxamic acid, $C_6H_5CONH.OCO.C_6H_5$. If, however, it is assumed that a triacylated hydroxylamine, constituted according to the true hydroxylamine type, *viz.*, $\begin{matrix} CH_3CO \\ C_6H_5CO \end{matrix}>N-O-CO.C_6H_5$, is also present, the formation of the benzoyl ester of benzhydroxamic acid becomes explicable, for of two groups bearing the same relation to the nitrogen atom, the acetyl group would be more readily affected by alcoholic potash than the benzoyl group.

The decomposition may be expressed thus :

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH. \qquad C_6H_5-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{\|}}{C}}-N-O-COC_6H_5.$$
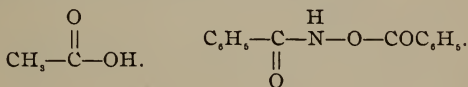
In order to establish the correctness of this interpretation, it was necessary to study the action of benzoyl chloride on the sodium salt of the benzoyl ester of acethydroxamic acid, $CH_3-C\begin{cases} ONa \\ NOCOC_6H_5 \end{cases}$.
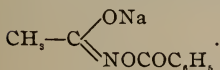
The Action of Benzoyl Chloride on the Sodium Salt of the Benzoyl Ester of Acethydroxamic Acid.

4.2 grams of the sodium salt, prepared as described above, were suspended in 38 grams of absolute ether, and 2.7 grams of benzoyl chloride (slightly less than 1 molecule) were added. The action commenced at once, and at the end of two days was complete.

The sodium chloride (1.2 grams) was filtered, and the ether solution evaporated ; a thick, colorless, syrupy oil remained in the evaporating-dish, weighing 5.4 grams. After standing for two weeks, exposed to the coldest winter temperature,

the oil showed signs of solidifying, and at the end of three weeks, the crystalline magma was transferred to a clay plate. The solid, freed from oil in this way, amounted to 2.5 grams. It was redissolved in a small quantity of ether, and warm ligroïn added, when, on cooling, it was deposited in large, transparent, well-developed crystals, melting at 68°–69°.

The oil was extracted from the pieces of clay plate by boiling ether; on evaporating the ether, a thick, oily substance remained, which showed no signs of solidifying after standing four weeks.

α-Benzoyl-β-acetylbenzoylhydroxylamine,

$$CH_3C \diagdown^{O} \atop C_6H_5C \diagup_{O} \rangle N - O - CO.C_6H_5.$$
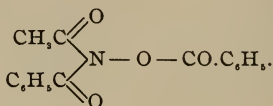
The solid, melting at 68°–69°, is a neutral substance, insoluble in alkalies, but decomposed by them quite readily. It is easily soluble in alcohol and ether, quite soluble in boiling ligroïn, sparingly soluble in cold ligroïn, and insoluble in water.

0.1327 gram gave 0.3307 gram CO_2, and 0.0560 gram H_2O.
0.1473 gram gave 6.8 cc. N_2 at 20° and 743.7 mm.

	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.95
H	4.62	4.68
N	4.94	5.15

The correctness of the formula assigned is shown by the behavior of the solid towards alcoholic potash, and more conclusively by its synthesis from the potassium salt of the benzoyl ester of benzhydroxamic acid and acetyl chloride, which will be considered later.

Behavior towards Alcoholic Potash.

The solid isomer is decomposed on treatment with alcoholic potash almost completely into the benzoyl ester of benz-

hydroxamic acid, $C_6H_5-C \overset{\displaystyle O}{\underset{\displaystyle NHOCOC_6H_5}{<}}$, and acetic acid

(or acetic ether). Not a trace of the benzoyl ester of acet-

hydroxamic acid, $CH_3-C \overset{\displaystyle O}{\underset{\displaystyle NHOCOC_6H_5}{<}}$, could be found.

1 gram of the crystalline isomer (melting-point 68°–69°) was dissolved in 20 grams of alcohol, and treated with alcoholic potash (0.4 KOH equivalent to 2 mols.). The crystalline salt which separated was filtered (0.4 gram), dissolved in water, and treated with carbon dioxide. In this way 0.38 gram of the benzoyl ester of benzhydroxamic acid, melting at 159°–160°, was obtained. It was identified by conversion into diphenylurea. The alcoholic filtrate was diluted with water, and extracted with ether. On distilling the ether extract, very small quantities of acetic ether, and benzoic ether were recognized by their odors. The diluted alcoholic solution was then acidified with dilute sulphuric acid; from this solution ether extracted 0.45 gram of the benzoyl ester of benzhydroxamic acid, containing traces of benzoic acid. This amount (0.45 gram), redissolved in sodium hydroxide and precipitated by carbon dioxide, gave 0.4 gram of pure acid, melting at 158°.

The acidified solution, from which these substances had been extracted, gave a reaction with ferric chloride for benzhydroxamic acid, $C_6H_5-CO.NHOH$, which was formed by the further decomposition of the benzoyl ester of benzhydroxamic acid; this explains the presence of traces of benzoic acid and benzoic ether.

In all, 0.76 gram of the benzoyl ester of benzhydroxamic acid were obtained instead of 0.85 gram, the calculated amount.

Benzoyl Ester of Benzoylacethydroximic Acid,

$$CH_3-C \overset{\displaystyle O-CO.C_6H_5}{\underset{\displaystyle N-O-CO-C_6H_5}{<}}.$$
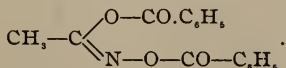
The oily isomer obtained in the above reaction shows a

totally different behavior towards alcoholic potash. It is decomposed almost entirely into the benzoyl ester of acethydroxamic acid, $CH_3—C=O.NH.O.COC_6H_5$, and benzoic acid (or ethyl benzoate), which establishes the constitutional formula assigned. 0.9 gram of the oily isomer, treated with alcoholic potash (0.35 gram KOH in 17 grams alcohol) in exactly the same manner as the solid isomer, gave the following results:

		Gram.
Benzoyl ester of acethydroxamic acid,	$CH_3—C{<}^{O}_{NHOCOC_6H_5}$	0.5
Ethyl benzoate,	$C_6H_5.COOC_2H_5$	0.3
Benzoic acid,	C_6H_5COOH	trace
Benzoyl ester of benzhydroxamic acid,	$C_6H_5—C{<}^{O}_{NHOCOC_6H_5}$	0.08

The formation of this last substance is to be accounted for by the presence of some of the solid isomer dissolved in the oil.

The neutral oil obtained from sodium isonitroethane, therefore, behaves in every respect as a mixture of almost equal quantities of these two isomers. It is not strange that this oil has resisted all attempts to solidify it, when we consider its method of preparation, and the fact that it contains slight impurities, such as ethyl benzoate and nitroethane. Furthermore, the product obtained by the action of the sodium salt of pure benzoyl ester of acethydroxamic acid and benzoyl chloride solidified but partially, and then only after an exposure of three weeks to extreme cold, accompanied by the usual scratching to facilitate crystallization.

It is only possible to explain the formation of the two isomers from the sodium salt of benzoyl ester of acethydroxamic acid and benzoyl chloride, by assuming that two processes are taking place side by side; namely, direct replacement of the metal by the benzoyl group, and the addition of benzoyl chloride to the sodium salt, with subsequent loss of sodium chloride.

I. $CH_3-C\underset{NOCOC_6H_5}{\overset{ONa}{\big<}} + C_6H_5CO.Cl =$

$CH_3-C\underset{N-O-COC_6H_5}{\overset{O-CO-C_6H_5}{\big<}} + NaCl.$

II. $CH_3-C\underset{NO.CO.C_6H_5}{\overset{O-Na}{\big<}} + C_6H_5COCl =$

$$CH_3-\underset{\underset{C_6H_5}{\overset{|}{CO}}}{\overset{O-Na}{\underset{|}{C}}}-\underset{|}{N}-O-CO.C_6H_5.$$
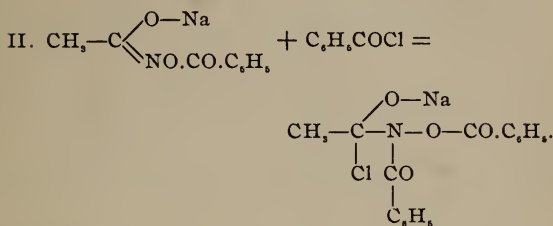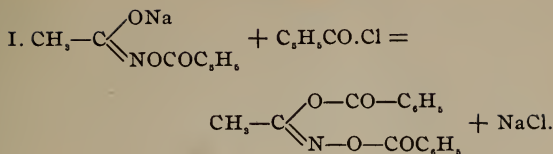
By loss of sodium chloride the last product becomes

$$\underset{C_6H_5C}{\overset{CH_3C}{\big<}}\overset{O}{\underset{O}{\big>}}N-O-CO-C_6H_5.$$
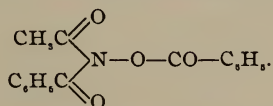
In order to establish the correctness of this explanation, the following experiment was carried out: Acetyl chloride was allowed to act on the potassium salt of the benzoyl ester of benzhydroxamic acid, $C_6H_5-C\underset{N-O-CO.C_6H_5}{\overset{OK}{\big<}}$.

It is evident that if addition does occur, the addition-product formed in this case must be identical with the solid isomer (melting-point 68°–69°) obtained by the addition of benzoyl chloride to the sodium salt of the benzoyl ester of acethydroxamic acid. This conclusion is borne out by experiment.

The Action of Acetyl Chloride on the Potassium Salt of the Benzoyl Ester of Benzhydroxamic Acid, $C_6H_5-C\underset{N-O.CO.C_6H_5}{\overset{OK}{\big<}}$.
—The benzoyl ester of benzhydroxamic acid used was pre-

pared according to Lossen's[1] method from hydroxylamine and benzoyl chloride.

11 grams of the potassium salt were suspended in absolute ether, and treated with 3.1 grams (1 mol.) of acetyl chloride. In twelve hours the action was complete. After removing the sodium chloride, the ether solution was placed in a glass evaporating-dish and the ether evaporated *in vacuo.* Thus, 8.2 grams of solid, crystalline material, with traces of oil, were obtained. The oil was removed by placing the solid on a clay plate, and was not investigated. The solid was crystallized as follows: Boiling ligroïn (40°–60°) dissolved it, with the exception of 0.5 gram of regenerated benzoylhydroxamic acid. On cooling, the ligroïn solution was filled with radiating groups of long, needle-shaped crystals, and at the same time short, thick, transparent crystals formed on the sides of the crystallizing flask. After filtering, these crystals were separated by selection. 3.7 grams of needle-shaped crystals, melting at 84°–85°, and 1.7 grams of transparent crystals, melting at 68°–69°, were obtained.

Solid Melting at 68°–69°.—This substance is identical in every respect with α-benzoyl-β-acetylbenzoylhydroxylamine,

$$\begin{array}{c} CH_3CO \\ C_6H_5CO \end{array}\!\!\!\!\Big\rangle N{-}O{-}CO.C_6H_5,$$ obtained from the benzoyl ester

of acethydroxamic acid.

0.1443 gram gave 0.3583 gram CO_2, and 0.0610 gram H_2O.
0.2545 gram gave 11.2 cc. N_2 at 22° and 753.8 mm.

	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.75
H	4.62	4.69
N	4.94	4.96

Behavior towards Alcoholic Potash.—0.9 gram dissolved in 17 grams of alcohol, and treated with a solution of potassium hydroxide, containing 3.5 grams, gave 0.7 gram of the benzoyl ester of benzhydroxamic acid, $C_6H_5C\!\!\Big\langle\begin{array}{c} O \\ NHOCOC_6H_5 \end{array};$ calculated 0.76 gram.

[1] Ann. Chem. (Liebig), **161**, 347.

A crystallographic comparison of crystals of this preparation with those obtained from the benzoyl ester of acethydroxamic acid and benzoyl chloride was carried out in Prof. Groth's laboratory at Munich by Mr. Zirngiebl, to whom I wish to express my obligation for his kindness. The complete identity of the two specimens is established.

Crystal system : monoclinic.

$$a : b : c = 1.3064 : 1 : 1.0390.$$

$$\beta = 107°22'.$$

The forms observed are : 010, 100, 001, $11\bar{1}$, $10\bar{1}$.

$$001 \ : \ 100 \ = \ 72°38'$$

$$\bar{1}11 \ : \ \bar{1}00 \ = \ 70°36'$$

$$\bar{1}11 \ : \ \overline{1}\overline{1}1 \ = \ 87°59'$$

Cleavage 001.   Plane of the optical axes $\perp$ 010.

Benzoyl Ester of Acetylbenzhydroximic Acid,
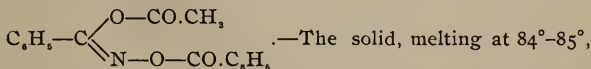
$C_6H_5{-}C\Big\langle{\overset{\displaystyle O-CO.CH_3}{N-O-CO.C_6H_5}}$.—The solid, melting at 84°-85°, obtained in the same reaction, is formed by the direct replacement of the metal by the acetyl group. It is a neutral substance, soluble in ether, and alcohol, very slightly soluble in cold ligroïn, quite readily in warm ligroïn, and insoluble in water.

0.0602 gram gave 0.1494 gram CO_2, and 0.0265 gram H_2O.
0.2240 gram gave 9.7 cc. N_2 at 25° and 749.7 mm.

	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.68
H	4.62	4.88
N	4.94	4.79

The following equations will explain the formation of these substances :

I. $C_6H_5-C\begin{smallmatrix}OK\\NOCOC_6H_5\end{smallmatrix}$ + $CH_3COCl =$

$C_6H_5-C\begin{smallmatrix}O-CO.CH_3\\N-O-CO.C_6H_5\end{smallmatrix}$ + KCl.

II. $C_6H_5-C\begin{smallmatrix}OK\\N-O-CO.C_6H_5\end{smallmatrix}$ + $CH_3-COCl =$

$C_6H_5-C-N-O-CO.C_6H_5$ with OK above C, Cl and CO below, CH_3 below CO.
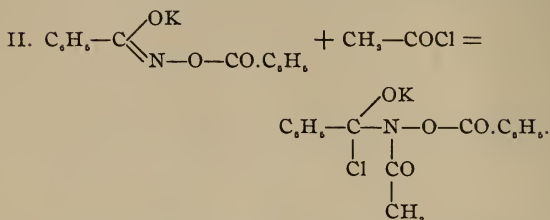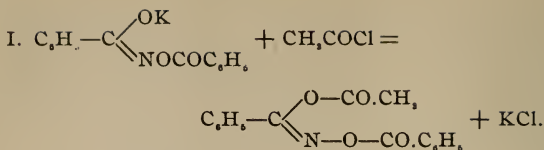
This addition-product loses potassium chloride giving

$\begin{smallmatrix}C_6H_5C\\CH_3C\end{smallmatrix}\begin{smallmatrix}O\\ \\O\end{smallmatrix}N-OCOC_6H_5.$
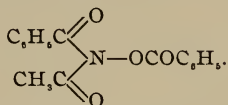
These reactions seem to throw some light upon the nature of the triacylated hydroxylamine derivatives in general. It has been established that compounds of this class exist in more than one form; in no case, however, in more than three forms. Lossen[1] has preferred to regard them as physical isomers, not, however, denying the possibility of considering them as space isomers. Hantzsch and Werner suggested the possibility of interpreting them from the standpoint of geometrical isomerism, depending upon the presence of an oxime grouping. Werner[2] has since established the presence of such isomeric relations among the hydroximic acid derivatives, as, for example, α- and β-ethylhydroximic acid, which he showed to be related as *syn* and *anti* forms,

$C_6H_5-C-O-C_2H_5$ with $\parallel$ and $H-O-N$ below. $C_6H_5-C-O-C_2H_5.$ with $\parallel$ and $N-O-H$ below.

1 Ann. Chem. (Liebig), **186**, 1; **252**, 170; **265**, 176; **281**, 169.
2 Ber. d. chem. Ges., **25**, 27; **26**, 1562, 1567; **29**, 1153.

This, however, accounts for only two forms, and in some cases three are known. It has often been suggested that the third form may correspond to a true hydroxylamine type, $\begin{array}{c}\text{RCO} \\ \\ \text{RCO}\end{array}\Big\rangle\text{N—O—COR}$; but experimental evidence was lacking to confirm this view. The results, presented above, prove conclusively that compounds of this type can exist. It still remains to be determined whether even this explanation is sufficient to account for all the cases of isomerism, and the many intricate relations observed in the study of the hydroxamic and hydroximic acids.
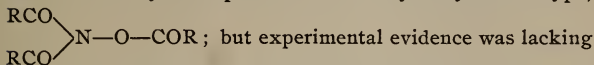
Explanation of the Reaction of Benzoyl Chloride with Sodium Isonitroethane.

Having considered this reaction in all its details, it is now possible to sum up the results, and to formulate the course of the action in the following equations. By the direct replacement of the metal by benzoyl, a derivative of isonitroethane results :

$$CH_3—CH{=}N{-}O{-}Na + C_6H_5—COCl =$$
$$\underset{\underset{O}{\|}}{}$$

$$CH_3—CH{=}N{-}O{-}CO.C_6H_5 + NaCl.$$
$$\underset{\underset{O}{\|}}{}$$
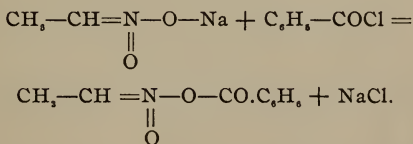
This substance cannot be isolated, but is immediately converted by intramolecular oxidation into the benzoyl ester of acethydroxamic acid,

$$CH_3—CH{=}N{-}O{-}CO.C_6H_5 \;\longrightarrow\; CH_3—C\!\!\begin{array}{l}\diagup OH \\ \diagdown N{-}O{-}CO.C_6H_5\end{array}$$
$$\underset{\underset{O}{\|}}{}$$
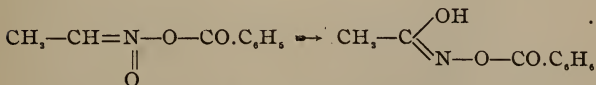
Being a stronger acid than isonitroethane, it immediately reacts with the isonitroparaffin salt, regenerating nitroethane, and forming the sodium salt of the benzoyl ester of acethydroxamic acid,

$$CH_3CH = N - O - Na + CH_3 - C \underset{N-O-CO.C_6H_5}{\overset{OH}{<}} =$$

$$CH_3 - CH_2 - NO_2 + CH_3 - C \underset{NOCOC_6H_5}{\overset{ONa}{<}}.$$
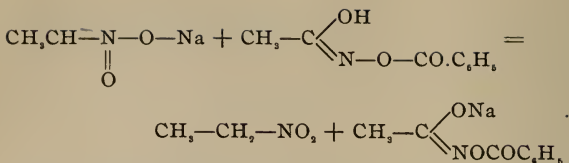
In the presence of benzoyl chloride, this salt reacts just as the synthetic salt was found to act, namely, in two ways, by addition; and by direct replacement, forming dibenzoylacethydroximic acid, and α-benzoyl-β-acetylbenzoylhydroxylamine :

$$\text{I.} \quad CH_3 - C \underset{NOCOC_6H_5}{\overset{ONa}{<}} + C_6H_5 - COCl =$$

$$CH_3 - C \underset{N-O-CO.C_6H_5}{\overset{O-CO.C_6H_5}{<}} + NaCl.$$

$$\text{II.} \quad CH_3 - C \underset{NOCOC_6H_5}{\overset{ONa}{<}} + C_6H_5 - COCl =$$

$$CH_3 - \underset{\underset{\underset{C_6H_5}{|}}{\overset{|}{CO}}}{\overset{ONa}{\underset{|}{\overset{|}{C}}}} - NOCOC_6H_5 = \underset{C_6H_5C \overset{O}{\underset{O}{<}}}{\overset{CH_3C \overset{O}{<}}{}} N - O - COC_6H_5 + NaCl.$$
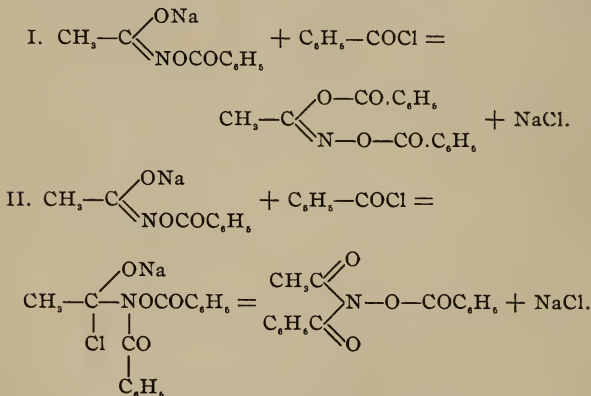
2. *The Action of Chlorcarbonic Ether on Sodium Isonitroethane.*

This reaction has not been studied as thoroughly as the action of benzoyl chloride on sodium isonitroethane. The evolution of large amounts of carbon dioxide introduces a complication which was not foreseen, and although the resulting neutral oil contains derivatives of acethydroxamic acid, it has not been found possible to determine the exact nature of these substances.

22.3 grams of chlorcarbonic ether were allowed to act on 20 grams of sodium isonitroethane, suspended in 120 grams of

absolute ether; 3.2 grams of carbon dioxide were evolved, and a residue remained which weighed 16.9 grams, and was composed of sodium chloride (66 per cent.), sodium carbonate, and some sodium nitrate. The ether gave, on evaporation, 11.2 grams of reddish, neutral oil. A loss of material had occurred amounting to 11 grams; this was due chiefly to nitroethane, and amounts to a little more than half of the sodium nitroethane used.

Properties of the Neutral Oil.—It is sparingly soluble in water. On heating a few drops with sodium hydroxide and acidifying with dilute sulphuric acid, an evolution of carbon dioxide occurred, and ferric chloride gave an intense cherry-red color reaction, identical with the test given by acethydroxamic acid. When alkalies are added to the oil, the red color characteristic of salts of ethylnitrolic acid is produced; this disappears on acidifying, and is regenerated by fresh alkali.

After standing for several weeks, the oil showed no signs of solidifying. It suffers considerable decomposition when distilled even under diminished pressure. When distilled at ordinary pressure, a portion passes over below 170°; the remainder between 200° and 230°. Carbon dioxide is evolved, and the distillate possesses an intense odor of isocyanate. A few drops of the higher-boiling fraction, heated with alkali, gave, on acidifying, an intense reaction with ferric chloride; this shows that the derivatives of acethydroxamic acid distilled, at least in part, without decomposition.

Synthesis of the Carbethoxyl Ester of Acethydroxamic Acid,

$$CH_3—C{\overset{\displaystyle /\!\!/O}{}}—\underset{H}{N}—O—CO_2C_2H_6.$$—It was expected that the action
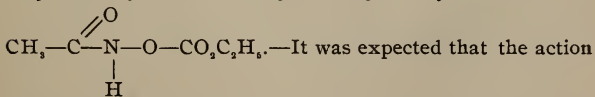
of chlorcarbonic ether on sodium isonitroethane would give results corresponding to those obtained by the action of benzoyl chloride. It was necessary, therefore, to become familiar with the carbethoxy derivatives of acethydroxamic acid, and of ethylnitrolic acid. These have been prepared synthetically.

Six grams of acethydroxamic acid were dissolved in a few

cubic centimeters of cold water, and, after neutralizing with one molecule of potassium hydroxide, one molecule of chlorcarbonic ether was added. In a few minutes the reaction was complete; the clear solution was extracted with ether, the ether dried with calcium chloride, and partially distilled. The remainder, poured into an evaporating-dish, left, on evaporation, a snow-white crystalline mass, which, after drying on a clay plate to remove traces of chlorcarbonic ether, weighed 4.1 grams. Crystallized from ether and ligroïn (40°–60°), it separates in long, flat needles, with a shining, pearly luster, and melts at 71°–72°.

0.2700 gram gave 0.4039 gram CO_2, and 0.1507 gram H_2O.
0.1875 gram gave 15.2 cc. N_2 at 13°.5 and 756.4 mm.

	Theory for $C_5H_9NO_4$.	Found.
C	40.81	40.79
H	6.12	6.20
N	9.52	9.53

Properties of the Carbethoxyl Ester of Acethydroxamic Acid.— It is readily soluble in ether, alcohol, and water, soluble in benzol, and chloroform, almost insoluble in ligroïn. A water solution, when first prepared, gives no reaction with ferric chloride, but on standing several hours it shows an intense color reaction. It is readily decomposed by alkalies, and alkaline carbonates, acethydroxamic acid being formed. Towards acids it is much more stable.

Its behavior on distillation resembles, in some respects, the behavior of the neutral oil obtained by the action of chlorcarbonic ether on sodium isonitroethane; carbon dioxide is evolved, an intense odor of isocyanate is observed, and a pale yellow oil distils between 180°–220°.

Synthesis of the Carbethoxyl Ester of Ethylnitrolic Acid,
$$CH_3-C{\underset{N-O-CO_2C_2H_5}{\overset{NO_2}{}}}$$
.—2.4 grams of the ethylnitrolic acid, prepared from nitroethane, were dissolved in 25 cc. of water; 0.9 gram of potassium hydroxide, and 2.5 grams of chlorcarbonic ether were added. The red color of the solution soon disappeared, and a yellow oil separated.
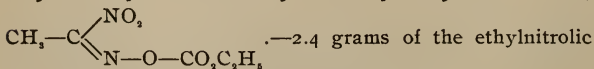
The solution and yellow oil were extracted with ether, the ether dried with calcium chloride, and distilled; 2.1 grams of the oil were obtained by distillation at reduced pressure, boiling at 143°–144° under 17 mm.

0.1720 gram gave 0.2187 gram CO_2, and 0.0719 gram H_2O.

	Theory for $C_5H_8N_2O_5$.	Found.
C	34.09	34.67
H	4.54	4.64

Properties.—It is a pale yellow oil, slightly soluble in water. Boiling water decomposes it, liberating carbon dioxide, and forming ethylnitrolic acid and its decomposition-products. In the presence of alkalies, it is readily decomposed, an intense red solution of salts of ethylnitrolic acid being formed. It boils at ordinary pressures, with considerable decomposition, at 210°–215°.

The presence of this substance in the neutral oil obtained by the action of chlorcarbonic ether on sodium nitroethane, accounts for the formation of salts of ethylnitrolic acid, on treating this oil with alkalies.

3. *The Action of Benzoyl Chloride on Sodium Isonitromethane.*

This reaction still presents difficulties, which have not been overcome. The action seems to proceed in a different manner, depending upon the kind of salt used, that is, whether the alcoholate, $CH_2=NONa, C_2H_5OH$, or the alcohol-free salt is
$$\overset{\|}{O}$$
used.

In all cases, the chief product of the reaction is a neutral oil. 20 grams of the sodium isonitromethane[1] (alcohol-free) and 33

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[1] A curious observation in this connection with nitromethane may be mentioned here. Kahlbaum's nitromethane was used, and its purity established by distillation. It was perfectly transparent, and free from color when first obtained; but, on exposure to the light for some time, it gradually assumed a pale yellow tinge, and an odor identical with that of *prussic acid* was noticed. Could this have been due to the formation of fulminic acid, $H—O—N\equiv C$, by oxidation :

$$H_3C—NO_2 + H_2O = H_3CN\underset{\displaystyle\overset{\|}{O}}{\overset{\displaystyle OH}{<}} OH = H_2C=NOH + H_2O ?$$
$$\overset{\|}{O}$$
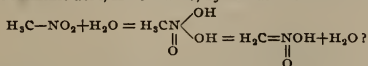
This isonitromethane, by intramolecular oxidation, could yield formhydroximic acid, and this, by loss of water, fulminic acid :

$$H_2C=NOH = HC\overset{\displaystyle OH}{\underset{\displaystyle NOH}{<}} = C=N—OH + H_2O.$$
$$\overset{\|}{O}$$
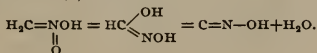
grams of benzoyl chloride in 180 grams of absolute ether, gave 19.8 grams of reddish, neutral oil. The solid residue weighed 17.2 grams, and contained, in addition to sodium chloride, a considerable quantity of sodium benzoate. The sodium bicarbonate, and sodium hydroxide extracts gave 5.3 grams of benzoic acid. A loss, therefore, of 10.7 grams of material had occurred, which was due to regenerated nitromethane.

Properties of the Neutral Oil.—The oil could not be solidified. Complete decomposition ensued on attempting to distil it, even at reduced pressure; benzoic acid, and isocyanate were formed. Concentrated hydrochloric acid decomposed it, forming large quantities of benzoic acid (3 grams of oil gave 2.6 grams of benzoic acid), small amounts of formic acid (identified as lead salt), and some hydroxylamine hydrochloride (identified as acetoxime). When heated with dilute alkalies, it suffers decomposition; benzoic acid is deposited on acidifying, and the solution gives an intense reaction with ferric chloride, identical with the color reaction obtained with formhydroxamic acid, $H-C\diagup_{\diagdown NHOH}^{O}$, which has been synthetically prepared, and will be described later.

Behavior towards Alcoholic Potash.—6 grams of this neutral oil, treated with alcoholic potash in the manner described in connection with the neutral oil obtained from nitroethane, gave 3.2 grams of potassium benzoate, 2.5 grams of ethyl benzoate, 1 gram of benzoic acid, and 0.3 gram of the benzoyl ester of formhydroxamic acid, $H-C\diagup_{\diagdown NHOCO.C_6H_5}^{O}$. The mixture of benzoic acid and the benzoyl ester of formhydroxamic acid extracted from the acidified alcoholic solution by ether was treated with boiling ligroïn to remove benzoic acid, and the remaining benzoyl ester of formhydroxamic acid purified by recrystallizing from ether and ligroïn. It separated in transparent crystals, melting at 76°–77°, identical with the crystals of this substance prepared synthetically from formhydroxamic acid and benzoyl chloride, which will be described in connection with formhydroxamic acid.

The formation of this substance, by the action of alcoholic potash on the neutral oil, confirms the presence of the benzoyl ester of benzoylformhydroxamic acid in the oil. It is, therefore, evident that the action of benzoyl chloride on sodium nitromethane proceeds, at least in part, according to the following equations :

$$H_2C=N—ONa + C_6H_5—COCl = H_2C=N—O—CO.C_6H_5.$$
$$\quad\quad \overset{\|}{O} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \overset{\|}{O}$$
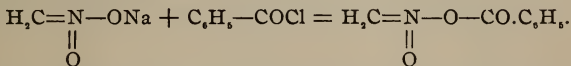
By oxidation this is converted into the benzoyl ester of formhydroxamic acid, $H—C\begin{smallmatrix} OH \\ NOCOC_6H_5 \end{smallmatrix}$, which decomposes sodium isonitromethane, forming the sodium salt of the benzoyl ester of formhydroxamic acid, and liberating nitromethane:

$$HC\begin{smallmatrix} OH \\ NOCOC_6H_5 \end{smallmatrix} + CH_2=NONa = H—C\begin{smallmatrix} ONa \\ NOCOC_6H_5 \end{smallmatrix} +$$
$$\overset{\|}{O}$$
$$CH_3—NO_2.$$
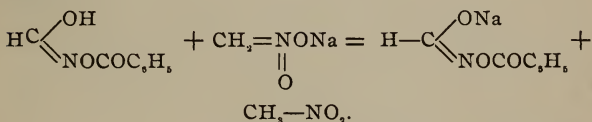
This salt then reacts with benzoyl chloride exclusively by direct replacement :

$$H—C\begin{smallmatrix} O—Na \\ NOCOC_6H_5 \end{smallmatrix} +C_6H_5COCl = H—C\begin{smallmatrix} OCOC_6H_5 \\ N—O—COC_6H_5 \end{smallmatrix},$$
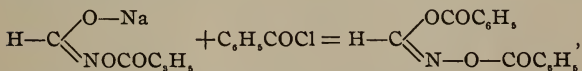
forming the benzoyl ester of benzoylformhydroxamic acid. That addition does not take place in this reaction is proved by the fact that in no case has it been possible to obtain the benzoyl ester of benzhydroxamic acid, $C_6H_5CO—NH—O—COC_6H_5$, as one of the decomposition-products of the neutral oil.

Synthesis of Formhydroxamic Acid, $H—\overset{\overset{O}{\|}}{C}—\underset{\underset{H}{|}}{N}—O—H,$ *and*

its Benzoyl Derivatives.

It was expected that the chief products of the action of ben-

zoyl chloride on sodium isonitromethane would be benzoyl derivatives of formhydroxamic acid.

In order to become familiar with the properties of these substances, it was necessary first to prepare synthetically formhydroxamic acid, the simplest of the hydroxamic acids.

$$\textit{Formhydroxamic Acid}, \ H-\overset{\overset{\textstyle O}{\|}}{C}-\underset{\underset{\textstyle H}{|}}{N}-OH.$$—A brief mention
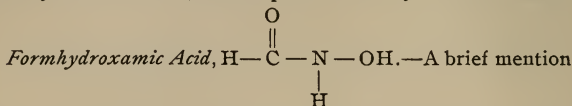
is made by Miolati[1] of a copper salt of formhydroxamic acid, but he does not describe any attempts to isolate the free acid. After several trials, the following method of preparation has been found to be the most satisfactory :

30 grams of hydroxylamine hydrochloride were dissolved in 150 cc. of boiling methyl alcohol, and to this solution, still warm, a solution of sodium methylate, containing 9.9 grams of sodium, was added. After mixing, the flask was cooled, and finally allowed to stand in a freezing-mixture for some time. The sodium chloride was filtered off, and the alcoholic solution of hydroxylamine distilled at reduced pressure, until two-thirds of the alcohol had distilled over.

After removing a small amount of sodium chloride, which had been deposited during the distillation, by filtering through glass wool, the solution was cooled to o°, and 31 grams of formic ether added directly. A slight elevation in temperature was observed, which was moderated by shaking, and cooling with running water. After standing for several hours at the temperature of the room, the mixture was placed in a glass evaporating-dish, and the methyl alcohol removed by evaporating in a vacuum-desiccator. 20 grams of crystalline material, containing some oil, and a slight amount of sodium chloride remained. The oil was removed by pressing the residue on a clay plate. Thus 17.9 grams of almost pure formhydroxamic acid were obtained, which was freed from the small quantity of sodium chloride by dissolving in pure ethyl acetate (free from acetic acid and water), heated to a temperature near its boiling-point. If

[1] Ber. d. chem. Ges., **25,** 703.

heated too long, or too high, much decomposition results.

On cooling, pure formhydroxamic acid, melting at 81°–82°, separated in large, thin, transparent plates, with a brilliant, pearly luster, and striated surfaces.

0.1890 gram gave 0.1359 gram CO_2, and 0.0847 gram H_2O.
0.1765 gram gave 35.8 cc. N_2 at 17° and 743.4 mm.

	Theory for $H-C\overset{/\!/O}{\underset{\diagdown NHOH}{}}$.	Found.
C	19.67	19.60
H	4.91	4.98
N	22.95	23.09

Properties of Formhydroxamic Acid.—It is insoluble in chloroform, ligroïn, and benzol ; very slightly soluble in ether ; readily soluble in alcohol, and water. It is dissolved by warm acetone, and is deposited on cooling in groups of thick crystals. On standing in contact with acetone, however, these crystals redissolve, and suffer a decomposition, the nature of which has not been fully determined. If perfectly pure form-hydroxamic acid is required, it can be prepared best by using pure hydroxylamine, obtained by distillation according to the method of Lobry de Bruyn, instead of the concentrated alcoholic solution containing sodium chloride. A water solution of formhydroxamic acid, even in the presence of considerable mineral acid, gives an intense cherry-red color reaction with ferric chloride, differing very slightly in tint from the color obtained with acethydroxamic acid.

The pure acid is quite stable, is not hygroscopic, and can be kept in open vessels without decomposition ; in closed tubes, it soon undergoes decomposition. When heated to a temperature slightly above its melting-point, it explodes with a sudden puff, sending forth a cloud of vapor, possessing the peculiar odor of hydroxylamine. This decomposition seems to be due to a dissociation into carbon monoxide and free hydroxylamine :

$$H-C\overset{\diagup O}{\underset{\diagdown NHOH}{}} = CO + H_2NOH.$$
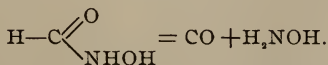
The stability of this substance is best explained by assign-

ing to it the oxam formula, $H—C \begin{smallmatrix} O \\ NHOH \end{smallmatrix}$; if the oxime

form, $H—C \begin{smallmatrix} OH \\ NOH \end{smallmatrix}$, were correct, this substance would lose

water spontaneously, and give fulminic acid :

$$\begin{smallmatrix} HO \\ H \end{smallmatrix} C = NOH = H_2O + C = NOH,$$
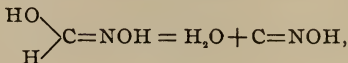
just as the oxime of formyl chloride, $\begin{smallmatrix} Cl \\ H \end{smallmatrix} C = NOH$, was found

to lose hydrochloric acid. It is, therefore, very probable, that the hydroxamic acids in the free state are constituted according to the oxam, and not according to the oxime type.[1]

Sodium Salt.—A sodium salt is formed by adding to an alcoholic solution of the acid one molecule of sodium ethylate. The alcohol must be absolute, otherwise the salt will separate as a gummy mass. A precipitate is first formed, which redissolves on adding the entire amount of sodium ethylate. This is probably an acid salt. From the alcoholic solution, the sodium salt is precipitated by adding absolute ether as a fine, white powder. The filtration and washing must be carried out very rapidly, as the salt is extremely hygroscopic. No analysis was made. Heated on a spatula, the salt explodes with a sharp puff, and a yellow flame. Salts are precipitated from its water solution by copper acetate, mercuric chloride, and lead acetate.

The copper salt is a dark green powder. The lead salt separates as a white, crystalline powder, which explodes on heating. The mercury salt, a deep yellow powder, explodes by percussion and on heating.

The Action of Benzoyl Chloride on the Salts of Formhydroxamic Acid.

To a solution of 10 grams of formhydroxamic acid in 50

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[1] The study of formhydroxamic acid, and its derivatives, especially in their relation to and conversion into fulminic acid and its esters, $RON = C$, will be continued in this laboratory.—J. U. NEF.

grams of cold water (5°), a solution of 6.5 grams of sodium hydroxide in 25 grams of water was added, and then benzoyl chloride, in small portions, until 23.3 grams were used. During the reaction the temperature was kept at 5°, and the flask shaken from time to time. A thick, gummy mass separated, and floated on the surface of the water. After shaking for ten minutes, the mixture was transferred to a separatory-funnel, and extracted with ether. Neutral and acid products were obtained by shaking the ether-extract first with a solution of sodium bicarbonate, then with a solution of sodium hydroxide. The remaining ether contained the neutral portion. The original water solution, after extraction with ether, gave an intense reaction with ferric chloride, showing the presence of large amounts of unchanged formhydroxamic acid.

Soluble in Sodium Bicarbonate.

Benzoyl Ester of Formhydroxamic Acid,

$$H-C \begin{matrix} \diagup\!\!\!\!O \\ \diagdown N-O-CO.C_6H_5 \\ | \\ H \end{matrix}$$
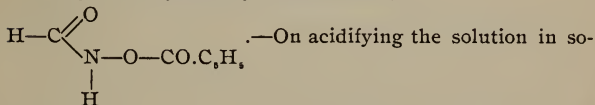
.—On acidifying the solution in sodium bicarbonate with dilute sulphuric acid, a colorless oil was formed. This was taken up by ether, the ether dried with calcium chloride, and evaporated; 7 grams of solid residue (no oil!) remained.

It is possible that in this case, also, two forms exist; the oil, which separated on acidifying, may correspond to the hydroximic acid type, $H-C \begin{matrix} \diagup OH \\ \diagdown NO-COC_6H_5 \end{matrix}$, which readily passes into the hydroxamic acid form, $H-C \begin{matrix} \diagup\!\!\!\!O \\ \diagdown NHOCOC_6H_5 \end{matrix}$.

A small amount of benzoic acid was removed by boiling ligroïn, and the remaining solid, 5.5 grams, which melted at 55°–60°, was dissolved in 50 cc. of absolute ether. On cooling, it crystallized in well developed, prismatic crystals, melting at 76°.5–77°.5. By addition of ligroïn it is completely precipitated from ether solution.

0.1250 gram gave 0.2662 gram CO_2, and 0.0487 gram H_2O.

0.1710 gram gave 12.9 cc. N_2 at 21° and 753 mm.

	Theory for $C_8H_7NO_2$.	Found.
C	58.18	58.08
H	4.24	4.32
N	8.48	8.54

Properties of the Benzoyl Ester of Formhydroxamic Acid.—
It is readily soluble in alcohol, less soluble in ether, almost
insoluble in ligroïn, and sparingly soluble in water. By so-
dium hydroxide it is decomposed, slowly in the cold, readily
on warming, into formhydroxamic acid and benzoic acid.
Heat decomposes it ; benzoic acid distils, and an intense odor
of isocyanate is observed. The substance is identical with
the benzoyl ester of formhydroxamic acid, obtained from nitro-
methane.

Soluble in Sodium Hydroxide.

Two grams of the benzoyl ester of benzhydroxamic acid,
$C_6H_5CONHOCOC_6H_5$, (melting at 159°–160°), were obtained
from the acidified solutions. Its formation is to be accounted
for by the partial decomposition of formhydroxamic acid into
carbon monoxide and hydroxylamine.

Neutral Portion.

Benzoyl Ester of Benzoylformhydroximic Acid,

$$H—C \Big\langle \begin{array}{l} OCO.C_6H_5 \\ N—O—CO.C_6H_5 \end{array}$$
.—Most of the ether was removed by
distillation. On pouring the remainder into an evaporating-
dish, 7.5 grams of crystalline solid separated. Recrystallized
from warm ether and ligroïn, it was obtained in delicate, col-
orless needles, melting at 109°–111°.

0.1407 gram gave 0.3443 gram CO_2, and 0.0553 gram H_2O.

0.2539 gram gave 12.2 cc. N_2 at 25° and 745 mm.

	Theory for $C_{15}H_{11}NO_4$.	Found.
C	66.91	66.74
H	4.08	4.36
N	5.20	5.28

Properties. — It is quite readily soluble in warm ether, and sparingly in cold ether, slightly soluble in warm ligroïn, and insoluble in water. It is insoluble in alkalies, but is decomposed by them, more readily on warming than in the cold. On acidifying, benzoic acid separates, and the solution gives an intense reaction with ferric chloride for formhydroxamic acid. The reaction may be represented by the following equations :

$$H-C \begin{matrix} \diagup O \\ \diagdown N-ONa \\ \quad | \\ \quad H \end{matrix} + C_6H_5COCl = $$
$$H-C \begin{matrix} \diagup O \\ \diagdown NHO.CO.C_6H_5 \end{matrix} + NaCl.$$
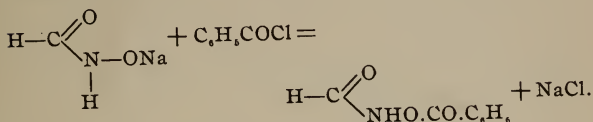
The benzoyl ester of formhydroxamic acid being a stronger acid than formhydroxamic acid, decomposes the sodium salt of the latter, setting free formhydroxamic acid,

$$H-C \begin{matrix} \diagup O \\ \diagdown NHONa \end{matrix} + H-C \begin{matrix} \diagup O \\ \diagdown NHOCO.C_6H_5 \end{matrix} = $$
$$H-C \begin{matrix} \diagup O \\ \diagdown NHOH \end{matrix} + H-C \begin{matrix} \diagup ONa \\ \diagdown N-OCO.C_6H_5 \end{matrix}.$$
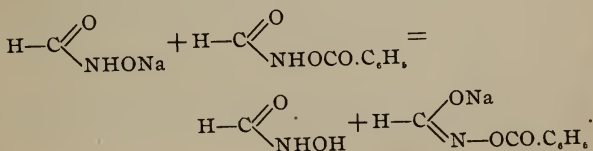
This sodium salt then reacts with benzoyl chloride,

$$H-C \begin{matrix} \diagup ONa \\ \diagdown NOCOC_6H_5 \end{matrix} + C_6H_5COCl = $$
$$H-C \begin{matrix} \diagup NOCOC_6H_5 \\ \diagdown NOCOC_6H_5 \end{matrix} + NaCl,$$
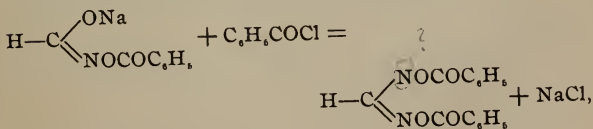
to give the benzoyl ester of benzoylformhydroximic acid.

Experiments with the Mercury Salt Obtained by the Action of Mercuric Chloride on Sodium Isonitromethane.

83 grams of sodium isonitromethane were dissolved in water, and, after cooling to 0°, a cold solution containing 121 grams of mercuric chloride was added. After standing two days, the white precipitate, which was at first deposited, be-

came yellow; it was boiled twice with water, filtered, and dried carefully on a clay plate. The product weighed 105 grams.

Many fruitless experiments were carried out with the salt and alkyl iodides. The mercury salt was supposed to be a basic mercury salt of carbon dioxide oxime, $H-O-N=C=O$,

to which Nef assigned the formula, $Hg\diagdown\diagup{}^{O}_{O}\diagup C=N-O-hg$.

It was hoped that esters of this acid, $R-O-N=CO$, would result.

A peculiar odor resembling that of prussic acid was observed by Nef, on treating this salt with dilute hydrochloric acid. In order to determine the nature of this substance, 10 grams of the mercury salt were heated with the calculated amount of dilute hydrochloric acid, and an attempt made to distil the volatile substance, and collect it in a well-cooled receiver. The yellow color of the salt disappeared, and a gray residue remained, weighing 3 grams. When a small portion of this residue was heated on a spatula, it exploded exactly like mercuric fulminate. It was redissolved in a solution of potassium cyanide, and precipitated, by adding dilute nitric acid, as a crystalline powder, identical with mercuric fulminate.

The original yellow salt is also soluble in potassium cyanide, but, if dilute nitric acid is added rapidly, not a trace of fulminate is obtained. It is, however, possible, by adding nitric acid drop by drop, to obtain mercuric fulminate from the solution of the salt in potassium cyanide.

The peculiar odor observed on treating the salt with dilute hydrochloric acid is due, therefore, to small quantities of

formyl chloride oxime, $HON=C\diagup{}^{H}_{Cl}$.

In view of the experiments with acid chlorides and isonitroparaffin salts, which have led, in all cases, to the formation of hydroxamic acid derivatives, it seems likely that, in the action of mercuric chloride on sodium isonitromethane, derivatives of formhydroxamic acid may be formed, as intermediate prod-

ucts in the synthesis of fulminates, discovered by Nef.[1] Thus,[2]

$$H_2C=N-O-Na + hgCl = H_2C=N-O-hg + NaCl.$$
$$\overset{\|}{O} \qquad\qquad\qquad \overset{\|}{O}$$

By oxidation,

$$H_2C=N-O-hg \;\longrightarrow\; H-C\!\!\begin{array}{l} \diagup OH \\ \diagdown N-O-hg \end{array}.$$
$$\overset{\|}{O}$$
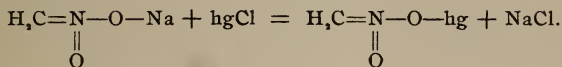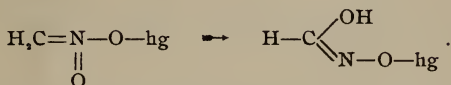
This salt of a hydroximic acid, before it can readjust itself to form a salt of a hydroxamic acid, $H-C\!\!\begin{array}{l} \diagup O \\ \diagdown N-O-hg \\ \qquad\; | \\ \qquad\; H \end{array}$, loses

water, giving rise to mercuric fulminate,

$$H-C\!\!\begin{array}{l} \diagup OH \\ \diagdown N-O-hg \end{array} = H_2O + C=N-O-hg.$$
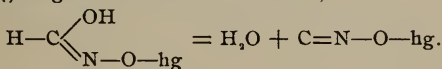
At the same time, by the further action of mercuric chloride, a basic mercury salt of formhydroximic acid results,

$$H-C\!\!\begin{array}{l} \diagup OH \\ \diagdown NOhg \end{array}.HgO, \qquad or \qquad H-C\!\!\begin{array}{l} \diagup O-Hg-OH \\ \diagdown N-O-hg \end{array}.$$
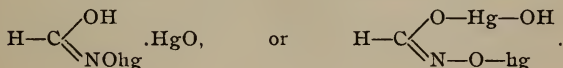
It is evident that on treating this basic salt with dilute hydrochloric acid, mercuric fulminate must be formed.

$$H-C\!\!\begin{array}{l} \diagup O-Hg-OH \\ \diagdown NOhg \end{array} + 2HCl = H-C\!\!\begin{array}{l} \diagup OH \\ \diagdown NOhg \end{array} + HgCl_2 +$$
$$H_2O;$$

$$H-C\!\!\begin{array}{l} \diagup OH \\ \diagdown N-O-hg \end{array} \;\longrightarrow\; H_2O + C=N-O-hg.$$
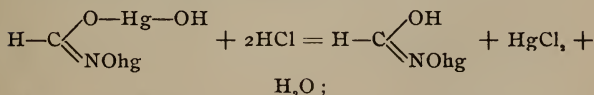
The analysis of the yellow mercury salt, made by Nef, agrees almost exactly with the theory for a basic mercury salt of formhydroxamic acid.

[1] Ann. Chem. (Liebig), 280, 270. [2] hg represents a half atom of bivalent mercury.

	Theory for $H-C\begin{smallmatrix}O-Hg-OH\\\\NOhg\end{smallmatrix}$	Found.
C	3.2	3.34
H	0.53	0.305
N	3.7	4.04
Hg	79.7	80.31

This interpretation is offered tentatively. It may be mentioned that a yellow mercury salt has been obtained by the action of mercuric chloride on the sodium salt of formhydroxamic acid, which resembles, in many respects, the peculiar salt described above. Both explode violently on heating, and by percussion.

The above experiments prove, in any case, that the yellow basic salts obtained from nitromethane cannot be derivatives of carbon dioxide oxime, as was considered probable by Nef; their behavior towards sodium amalgam, and other reagents, makes it improbable that they are basic fulminates. Their conversion into fulminates, as shown above, makes it possible to convert sodium isonitromethane almost quantitatively into mercuric fulminate.

Concerning the Formula of the Salts of the Nitroparaffins.

In assigning to the isonitroparaffins the open formula, $R-C=N-OH$, and excluding the ring grouping of

$$R-\overset{\underset{|}{H}}{\underset{\underset{O}{\vee}}{C}}-N-OH,[1]$$

Hantzsch, $R-C-N-OH$,[1] it was pointed out by Nef[2], that the latter formula does not explain the peculiar property, which these bodies possess, of undergoing intramolecular oxidation.

Many instances can be cited in which formulæ containing ring groupings have been assumed arbitrarily for which there is no experimental evidence. As examples of this kind, the following may be mentioned:

[1] Ber. d. chem. Ges., **29**, 699, 2251.   [2] *Ibid.*, **29**, 1218.

Nitrous oxide, $N{=}N$ instead of $N{\equiv}N{=}O$.
$$\underset{O}{\overset{\vee}{}}$$

Azoxy bodies, $R{-}N{=}NR$ instead of $R{-}N{=}N{-}R$.
$$\underset{O}{\overset{\diagdown\diagup}{}} \qquad \underset{O}{\overset{\|}{}}$$

Nitric acid, $HO{-}N{\big<}\!\!\begin{smallmatrix}O\\[-1pt]|\\[-1pt]O\end{smallmatrix}$ instead of $HO{-}N{\big<}\!\!\begin{smallmatrix}O\\[2pt]O\end{smallmatrix}$.

Nitramine salts, $R{-}N{-}NOM$ instead of $R{-}N{=}NOM$.
$$\underset{O}{\overset{\vee}{}} \qquad\qquad \underset{O}{\overset{\|}{}}$$

Isonitramine salt, $R{-}N{-}NOM$ instead of $R{-}N{=}NOM$.
$$\underset{O}{\overset{\vee}{}} \qquad\qquad \underset{O}{\overset{\|}{}}$$

The oxidation reactions may be grouped into two classes:

I. Cases in which the oxidation extends only to the adjacent carbon atom:

1. $R{-}CH{=}N{-}O{-}Ac$ (or M) $\rightarrow R{-}C{\big<}\!\!\begin{smallmatrix}OH\\[2pt]N{-}O{-}Ac(\text{or }M)\end{smallmatrix}$
   $$\underset{O}{\overset{\|}{}}$$

2. $2R{-}CH{=}N{-}O{-}H \rightarrow 2R{-}C{\big<}\!\!\begin{smallmatrix}H\\[2pt]O\end{smallmatrix} + N_2O + H_2O.$
   $$\underset{O}{\overset{\|}{}}$$
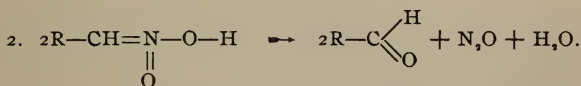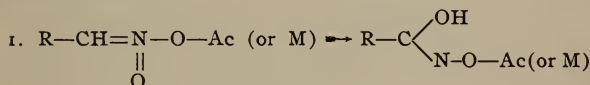
II. Cases in which the oxidation extends to carbon atoms not adjacent to the nitrogen atom:

$$\underset{\overset{\|}{O}}{\overset{\overset{\textstyle R}{|}}{R{-}C}}{=}N{-}OR \rightarrow \overset{\overset{\textstyle R}{|}}{R{-}C}{=}NOH + R{-}C{\big<}\!\!\begin{smallmatrix}O\\[2pt]H\end{smallmatrix}.$$
$$\text{(an aldehyde.)}$$
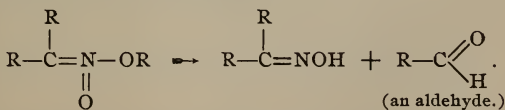
The oxidations belonging to Class I include all of the cases described in this paper; the formation of fulminates from nitromethane sodium;[1] and the peculiar decomposition of the salts of the nitroparaffins into an aldehyde (or ketone) and

[1] Ann. Chem. (Liebig), **280**, 263.

nitrous oxide, by the action of dilute acid, observed by Nef.[1]

Examples of the second class have been described by Nef.[2] Dinitroethane silver, $CH_3—C=N—O—Ag$, on treatment
$$\underset{NO_2\;\;O}{}$$

with alkyl iodides, gives results which can only be explained by admitting the formation of an ester, $CH_3—C = N—O—R$,
$$\underset{NO_2\;\;\;O}{}$$

which then decomposes, giving an aldehyde, and ethylnitrolic acid,

$$CH_3—\underset{\underset{NO_2\;O}{|\;\;\;||}}{C}=N—O—CH_2—R \rightarrow CH_3—\underset{\underset{NO_2}{|}}{C}=N—O—H + R—C\underset{H}{\overset{O}{<}}$$
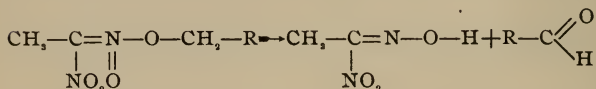
in the manner described by Nef. Another instance is found in the ethyl ester of fulminuric acid,

$$N\equiv C—\underset{\underset{C=O.NH_2}{|}}{C}=\!=\!=\!=\!=\!N—O—C_2H_5 \rightarrow$$

$$N\equiv C—\underset{\underset{CONH_2}{|}}{C}=N—O—H + CH_3—C\underset{H}{\overset{O}{<}},$$
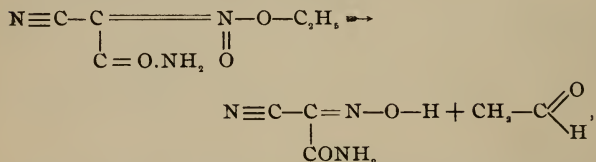
which, on boiling with water, gives acetic aldehyde, and cyan-isonitrosoacetamide.

It is impossible to see how these reactions are to be interpreted, if the ring grouping is adhered to.

II. Carbethoxyhydroxamic Acid (Oxyurethane),

$$C_2H_5O—C\underset{NHOH}{\overset{O}{<}}\text{, and its Alkyl and Acyl}$$
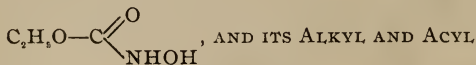
Derivatives.

In connection with the study of the mercury salt described above, attempts were made to obtain derivatives of the oxime of carbon dioxide, $HO—N=C=O$, from the salts and esters

[1] Ann. Chem. (Liebig), **280**, 266.
[2] *Ibid.*, **280**, 266.

of carbethoxyhydroxamic acid. If the salts possessed the form assigned by Lossen to the hydroxamic acids,

$$C_2H_5O—C\begin{smallmatrix} \diagup OH \\ \diagdown N—OM \end{smallmatrix}$$
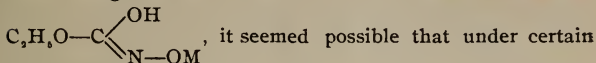
, it seemed possible that under certain conditions they would lose alcohol, and give rise to salts of the oxime of carbon dioxide. Many attempts were made to remove this alcohol, but without success.

The monoalkyl esters of carbethoxyhydroxamic acid were then prepared, $C_2H_5O—C\begin{smallmatrix} \diagup O \\ \diagdown NHOR \end{smallmatrix}$ (R = CH$_3$, C$_2$H$_5$, C$_7$H$_7$),
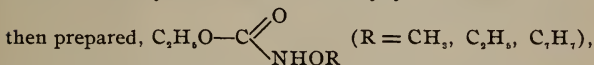
and preliminary experiments with these compounds have been carried out. It was expected that under the influence of phosphorus pentachloride, these esters would be decomposed, yielding hydrochloric acid, an alkyl chloride, and esters of the oxime of carbon dioxide, R—ON=C=O. These esters have not yet been isolated, but are undoubtedly formed in this way.

Carbethoxyhydroxamic Acid (Oxyurethane),

$C_2H_5O—C\begin{smallmatrix} \diagup O \\ \diagdown NHOH \end{smallmatrix}$.—This substance was first prepared by
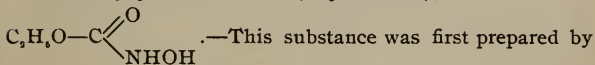
Hantzsch,[1] who obtained it by the action of hydroxylamine, in water solution, on chlorcarbonic ether, in the presence of sodium carbonate. The following modification of this method has been used, and found to give more satisfactory yields:

19.5 grams of hydroxylamine hydrochloride were finely powdered, and placed in a flask with 38 grams of powdered dry potassium carbonate. Enough ether was added to more than cover the mixture, and a few cubic centimeters of water. 30 grams of chlorcarbonic ether were then poured into the flask, a small portion at a time; the flask was cooled, and shaken until the violent solution of carbon dioxide moderated, and permitted the addition of another portion of chlorcarbonic ether. When the entire amount had been used, the flask was allowed to stand, being shaken from time to time, until the evolution of carbon dioxide ceased. The potassium

chloride was removed by filtration, the ether was washed once with water, dried with dehydrated sodium sulphate, and the ether distilled ; 26 grams of carbethoxyhydroxamic acid were obtained, equal to 89.6 per cent. of the theoretical yield.

Properties.—Prepared in this way it is identical with the oxyurethane described by Hantzsch.[1] It is a thick, colorless liquid, extremely soluble in water, and gives with ferric chloride an intense color reaction. On distillation, it was almost completely decomposed; at 180°–185° a colorless liquid distilled, which, on cooling, solidified to a mass of large, transparent plates, melting at 49°–50°. These were found to be urethane, $O=C{<}_{OC_2H_5}^{NH_2}$, (melting-point 49°–51°, boiling-point 184°).

Sodium Salt of Carbethoxyhydroxamic Acid,

$C_2H_5{-}O{-}C{<}_{NHONa}^{O}$. H_2O.—By adding sodium ethylate to an alcoholic solution of the acid, a sodium salt is precipitated as a white, crystalline powder, which detonates when heated to 110°.

0.2474 gram gave 0.1288 gram of Na_2SO_4.
0.2974 gram gave 0.1470 gram of Na_2SO_4.

	Theory for $C_3H_6NO_3Na + H_2O$.	Found. I.	II.
Na	15.86	16.8	16.0

This salt is readily soluble in water, and its solution reduces silver nitrate in the cold, and Fehling's solution on warming.

The Action of Methyl Iodide on Salts of Carbethoxyhydroxamic Acid.

To a solution of 29 grams of carbethoxyhydroxamic acid in methyl alcohol, a solution of 15.4 grams of potassium hydroxide in methyl alcohol, and 42 grams of methyl iodide were added. The separation of potassium iodide commenced at once, and it became necessary to cool the flask to prevent too great an elevation of temperature. After standing twenty-

[1] *Loc. cit.*

four hours, the potassium iodide was removed, and the methyl alcohol distilled under reduced pressure. The oil which remained, was dissolved in ether, and separated into neutral and acid portions by extracting the ether solution with dilute sodium hydroxide.

Soluble in Sodium Hydroxide.

Methyl Ester of Carbethoxyhydroxamic Acid,

$$C_2H_5O-C\begin{matrix}O\\\\NHOCH_3\end{matrix}$$.—After acidifying the alkaline extract

with dilute sulphuric acid, it was shaken out with ether, the ether dried and distilled. 9.2 grams of colorless liquid, boiling at 186°–188°, were obtained.

0.1372 gram gave 0.2047 gram CO_2, and 0.0953 gram H_2O.
0.2092 gram gave 21.7 cc. N_2 at 17° and 749.1 mm.

	Theory for $C_4H_9NO_3$.	Found.
C	40.33	40.61
H	7.56	7.70
N	11.76	11.90

Properties.—It is readily soluble in ether, alcohol, and water. When perfectly pure, it gives no reaction with ferric chloride, but traces of carbethoxyhydroxamic acid are sometimes present in the acid portion, and are carried over with the oil. In this case a reaction with ferric chloride is obtained, and the methyl ester is rendered impure by the presence of traces of urethane.

Decomposition by Concentrated Hydrochloric Acid.—1.4 grams of the methyl ester were heated with 10 cc. of concentrated acid in a sealed tube for an hour. On opening the tube, carbon dioxide and ethyl chloride escaped. The acid solution, evaporated to dryness on a water-bath, gave a crystalline residue, which dissolved completely in absolute alcohol. It was precipitated by absolute ether in white, crystalline flakes, melting at 148°–149°, identical in every respect with α-methyl-hydroxylamine hydrochloride, $CH_3ONH_2.HCl$, which melts at 149°.

0.0538 gram gave 0.0917 gram AgCl.

	Theory for CH_3ONH_2HCl.	Found.
Cl	42.51	42.46

Neutral Portion.

α-Methyl-β-Methylcarbethoxyhydroxylamine,

C_2H_5—O—C $\Big<^{\displaystyle O}_{\displaystyle N—O—CH_3}$ CH$_3$.—When the ether had passed off,
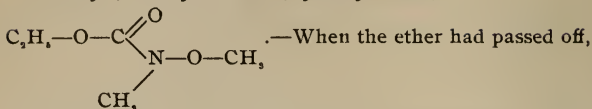
a colorless oil distilled at 150°–155°, weighing 4 grams. The neutral portion is formed in larger amounts when 2 molecules of potassium hydroxide, and 2 molecules of methyl iodide, are used; thus 22.5 grams of carbethoxyhydroxamic acid, 24 grams of potassium hydroxide, and 63 grams of methyl iodide, gave 2 grams of acid oil, methyl ester of carbethoxy-hydroxamic acid, boiling at 186°–188°, and 10.5 grams of neutral oil. In all cases considerable decomposition occurs.

A nitrogen determination showed that the oil was impure. 0.2410 gram (150°–153°) gave 19 cc. N_2 at 19° and 742 mm.

	Theory for $C_5H_{11}NO_3$.	Found.
N	10.52	8.88

The nature of this impurity has not been determined. It was at first expected that the neutral oil would contain alkyl derivatives of the carbethoxyhydroxamic acid of the form,
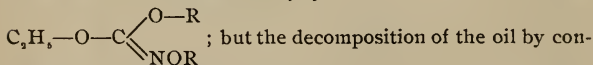
C_2H_5—O—C $\Big<^{\displaystyle O—R}_{\displaystyle NOR}$; but the decomposition of the oil by con-

centrated hydrochloric acid shows that the oil consists chiefly of *α*-methyl-*β*-methylcarbethoxyhydroxylamine, for not *α*-methylhydroxylamine hydrochloride, CH_3ONH_2HCl, but

α-dimethylhydroxylamine hydrochloride, $CH_3ON\Big<^{\displaystyle CH_3}_{\displaystyle H}$. HCl
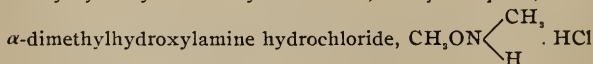
is formed.

In order to explain this reaction, we must assume that the alkyl iodide acts with the potassium salt of the methyl ester of carbethoxyhydroxamic acid by addition, and not by direct replacement.

$$C_2H_5-OC\diagdown_{N-O-CH_3}^{OK} + CH_3I = C_2H_5OC\diagdown_{\underset{\underset{CH_3}{|}}{\overset{|}{I}} N-O-CH_3}^{OK}.$$
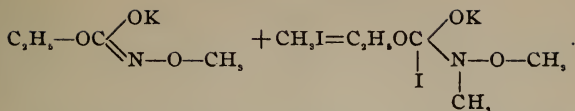
This product then loses potassium iodide, giving rise to α-methyl-β-carbethoxymethylhydroxylamine.

Decomposition of the Neutral Oil by Concentrated Hydrochloric Acid.

α-Dimethylhydroxylamine Hydrochloride,

$\underset{CH_3}{\overset{H}{\diagdown}}N-O-CH_3.HCl.$—Two grams of the oil (boiling-point 150°–155°), were heated in a sealed tube to 100° for thirty minutes with 10 cc. of concentrated hydrochloric acid. On opening the tube, carbon dioxide and ethyl chloride escaped. A crystalline salt, weighing 0.8 gram remained on evaporating the hydrochloric acid solution to dryness on a water-bath. The salt was soluble in alcohol, and precipitated from this solution by absolute ether, in small, shining plates, melting at 115°–116°. The best method of purifying it consists in dissolving the residue in boiling chloroform, from which it crystallizes, on cooling, in long, coarse, prismatic needles, melting at 115°–116°.

0.1209 gram gave 0.1086 gram CO_2, and 0.0894 gram H_2O.
0.1980 gram gave 24.5 cc. N_2 at 20° and 750.7 mm.
0.2097 gram gave 0.3057 gram of AgCl.
0.1049 gram gave 0.1555 gram of AgCl.

	Theory for $\underset{CH_3}{\overset{H}{\diagdown}}N-O-CH_3.HCl.$	Found.	
C	24.61	24.49	
H	8.20	8.21	
N	14.35	14.37	
Cl	36.41	35.71	36.65

Properties of α-Dimethylhydroxylamine Hydrochloride.—This salt is not hygroscopic, does not reduce ammoniacal silver nitrate; Fehling's solution is not reduced. It is quite volatile at the temperature of the water-bath, and considerable loss

occurs on evaporating its solution to dryness. The same similarity in solubility is noticed in the case of α-methylhydroxylamine and α-dimethylhydroxylamine hydrochlorides, that has been observed with the methylamine and dimethylamine hydrochloride; that is, the dimethyl derivatives in each case are soluble in chloroform, while the monomethyl derivatives are not.

α-*Dimethylhydroxylamine Chlorplatinate*, $(CH_3NHOCH_3)_2 \cdot PtCl_6$.—By adding platinic chloride, dissolved in alcohol, to an alcoholic solution of the hydrochloride, a solution of the chlorplatinate was obtained. Absolute ether precipitates the chlorplatinate as a deep orange-colored powder, melting with decomposition at 180°. It is obtained in red, prismatic crystals on recrystallizing from alcohol.

0.1341 gram gave 0.0510 gram Pt.

	Theory for $(CH_3ONHCH_3)_2PtCl_6$.	Found.
Pt	38.92	38.04

α-*Dimethylhydroxylamine*, $\begin{matrix} H \\ \diagdown \\ CH_3 \diagup \end{matrix} N{-}O{-}CH_3$.–Two grams of the hydrochloride, 5 grams of potassium hydroxide, and 10 grams of water, were placed in a small distilling-bulb, connected with a tube containing pieces of potassium hydroxide, and heated to 80° on a water-bath. The tube was connected with a condenser, through which ice-water circulated during the distillation. The free base (1 gram) was caught in a small distilling-bulb, cooled in a freezing-mixture, and redistilled, the same precautions being taken to cool the vapor. It boiled at 42°.2–42°.6.

0.1791 gram gave 0.2548 gram CO_2, and 0.1815 gram H_2O.
0.0734 gram gave 15.4 cc. N_2 at 19° and 737.8 mm.

	Theory for $\begin{matrix} H \\ CH_3 \diagup \end{matrix} N{-}O{-}CH_3$.	Found.
C	39.34	38.80
H	11.47	11.26
N	22.95	23.50

Properties of α-Dimethylhydroxylamine.—It is a colorless, extremely volatile liquid, possessing a sweet, rather unpleas-

ant basic odor, not in the least ammoniacal. It does not re-
duce silver nitrate or Fehling's solution. This furnishes a
method for preparing the α-dialkylhydroxylamines in a state
of purity, and avoids all of the difficulties encountered in their
preparation from α-monoalkylhydroxylamines by the action
of alkyl iodides.[1]

The study of these derivatives of carbethoxyhydroxamic
acid will be continued, with a view to preparing simple and
mixed α-dialkylhydroxylamines.

The Action of Ethyl Iodide on the Salts of Carbethoxyhydrox-amic Acid.

Twenty grams of carbethoxyhydroxamic acid, dissolved in
absolute alcohol, were treated with 10.7 grams of potassium
hydroxide, and 30 grams of ethyl iodide. After standing for
fifteen hours, the mixture was heated for ten minutes to a
temperature of 80°–90°, and, after cooling, filtered. The resi-
due was not pure potassium iodide, but contained some potas-
sium nitrite, and potassium carbonate.

The alcoholic solution was diluted with water, and extracted
with ether. The acid portion was removed from the ether
by means of dilute sodium hydroxide; the neutral products
remained dissolved in the ether.

Soluble in Sodium Hydroxide.

Ethyl Ester of Carbethoxyhydroxamic Acid,

$$C_2H_5-O-C\underset{NHOC_2H_5}{\overset{O}{\diagup\diagdown}}$$.—After acidifying the alkaline so-

lution, it was extracted with ether, and the ether dried with
calcium chloride. On distilling, 10 grams of the acid oil
were obtained, boiling at 195°–196° (95°–97° at 17 mm.).

0.1412 gram gave 0.2313 gram CO_2, and 0.1029 gram H_2O.
0.1615 gram gave 0.2651 gram CO_2, and 0.1208 gram H_2O.
0.1883 gram gave 18.5 cc. N_2 at 24° and 742.5 mm.

	Theory for $C_5H_{11}NO_3$.	I.	Found. II.	III.
C	45.11	44.67	44.77	....
H	8.27	8.09	8.30	....
N	10.52	....	....	10.82

[1] Lossen: Ann. Chem. (Liebig), **252**, 235.

Properties.—It is readily soluble in water, alcohol, and ether. Concentrated hydrochloric acid decomposes it; carbon dioxide is evolved, ethyl chloride, and α-ethylhydroxylamine hydrochloride are formed. The latter substance was precipitated from its alcoholic solution by ether in shining, pearly scales, melting at 127°–128°, which were found to be identical with α-ethylhydroxylamine hydrochloride prepared synthetically.

0.2597 gram gave 0.3825 gram AgCl.

	Theory for $C_4H_6ONH_2HCl$.	Found.
Cl	36.41	36.67

Action of Phosphorus Pentachloride on the Ethyl Ester of Carbethoxyhydroxamic Acid.—It was hoped that esters of the oxime of carbon dioxide, $RON{=}C{=}O$, would be formed by this means, but owing to the instability of the reaction-product, it has not been possible to decide whether esters of this form are present or not; the behavior of the product, however, seems to point to their presence.

On mixing the oil with phosphorus pentachloride, the action commences at once, and is greatly facilitated by gentle heat. Hydrochloric acid and ethyl chloride are evolved in large quantities, and a yellow oil remains in the distilling-bulb, mixed with phosphorus oxychloride. An attempt was made to distil this oil; when the oxychloride had passed off, and the thermometer still stood at 110°–115°, the liquid in the distilling-bulb began to turn brown, and with an enormous evolution of heat, passed into a dark-brown, carbonaceous residue.

If the reaction-product was poured directly into water, without attempting to distil it, a decomposition took place, carbon dioxide was evolved, and a clear solution resulted, from which only a few drops of oil could be extracted by ether. The water solution was made strongly alkaline by adding sodium hydroxide, and distilled, the distillate passing into a receiver containing dilute hydrochloric acid.

On evaporating the acid solution, almost the calculated amount of α-ethylhydroxylamine hydrochloride was obtained. Thus 5 grams of the ethyl ester of carbethoxyhydroxamic acid

gave 2.1 grams of hydroxylamine salt instead of 2.6 grams. This shows conclusively that the ethyl chloride evolved was not produced by the ethoxy group bound to nitrogen, but must have been formed by the ethoxy group bound to carbon. The study of this reaction will be continued.

Neutral Portion.

α-Ethyl-β-Ethylcarbethoxyhydroxylamine,

$$C_2H_5OC \underset{NOC_2H_5}{\overset{O}{<}}$$
$$\underset{C_2H_5}{/}$$
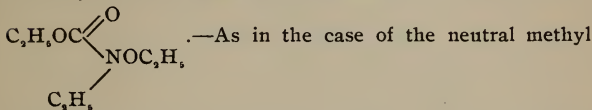
.—As in the case of the neutral methyl derivative, the ethyl derivative is impure. On evaporating the ether, an oil was obtained which boiled between 160° and 180°. Owing to the small amounts of this oil which have been prepared, a separation of the mixture by fractional distillation has not been tried. Its behavior towards concentrated hydrochloric acid shows that it consists essentially of the above compound, for not α-ethylhydroxylamine, but α-diethylhydroxylamine hydrochloride is found. The substance remains on evaporating the hydrochloric acid solution to dryness as a yellow oil, soluble in alcohol, and reprecipitated by ether as an oil. The same result was obtained on precipitating from alcohol by ligroïn. With dilute sodic hydrate it gives, on warming, a strong basic odor. It does not reduce Fehling's solution or ammoniacal silver nitrate. After standing in a desiccator in the cold for several weeks, it solidified partially to a mass of long, fibrous needles, which, after recrystallization from alcohol and ether, melted at 123°–124°.

The oily salt behaves just as α-diethylhydroxylamine hydrochloride, $C_2H_5\text{—O—N} \underset{H}{\overset{C_2H_5, HCl[1]}{<}}$, which has never, until now, been obtained in the solid form.

The Action of Benzyl Chloride on Carbethoxyhydroxamic Acid Salts.

27 grams of the carbethoxyhydroxamic acid, 11.9 grams of

[1] Lossen : Ann. Chem. (Liebig), **252**, 235.

potassium hydroxide, and 31 grams of benzyl chloride were dissolved in alcohol. Potassium chloride was deposited at once, and it was necessary to cool the flask, containing the mixture, to prevent too great a rise of temperature. After fifteen hours, the potassium chloride was removed by filtration, and after diluting the alcoholic solution with water, it was extracted with ether. The ether solution was shaken with dilute sodium hydroxide to remove acid products.

Soluble in Sodium Hydroxide.

Benzyl Ester of Carbethoxyhydroxamic Acid.

$$C_2H_5—O—C{\Large<}^{\textstyle O}_{\textstyle NHO—CH_2C_6H_5}$$
.—On acidifying the alkaline extract with dilute sulphuric acid, a light, colorless oil separated, and floated on the surface of the solution. This was extracted with ether, the ether dried and distilled. The residue was subjected to distillation at reduced pressure; 17 grams of colorless oil distilled at 171°–172° under 11 mm. pressure.

0.1562 gram gave 0.3523 gram CO_2, and 0.0958 gram H_2O.
0.2245 gram gave 13.9 cc. N_2 at 18° and 754.7 mm.

	Theory for $C_{10}H_{13}NO_3$.	Found.
C	61.53	61.51
H	6.61	6.82
N	7.18	7.13

Properties.—It is a thick, colorless oil, almost insoluble in water, readily soluble in alcohol and ether. It is soluble in alkalies, and is precipitated undecomposed by acids. On distilling at ordinary pressure, it suffers partial decomposition; a slight odor of benzaldehyde was observed.

Potassium Salt.—By adding alcoholic potash to an alcoholic solution of the acid, and precipitating with ether, the salt is obtained as a white, crystalline powder. It does not fuse at 260°. Heated in a tube, it decomposes, forming volatile, aromatic oils.

Sodium Salt.—The sodium salt was prepared by the action of sodium ethylate on an alcoholic solution of the acid. This

salt is much more soluble in alcohol than the potassium salt, and is not precipitated by ether.

The alcoholic solution was evaporated in a vacuum-desiccator; a colorless liquid remained, which redissolved on adding ether, and, after scratching with a glass rod, separated as a powder.

Action of Concentrated Hydrochloric Acid on the Benzyl Ester of Carbethoxyhydroxamic Acid.

It is decomposed by this reagent slowly in the cold, more readily on warming, and α-benzylhydroxylamine hydrochloride is deposited in pearly scales, which sublime above 220°. When treated with potassium cyanate, delicate needles of the urea derivative, $OC \big\langle \begin{smallmatrix} NHOC_7H_7 \\ NH_2 \end{smallmatrix}$, melting at 138°, were obtained.

The neutral oil, formed as a bye-product in the above experiment, boiled at 190°–215° at 15 mm.; it has not been investigated.

The Action of Benzoyl Chloride on Salts of Carbethoxyhydroxamic Acid.

Benzoyl Ester of Carbethoxyhydroxamic Acid,

$C_2H_5O - C \big\langle \begin{smallmatrix} O \\ NHOCO.C_6H_5 \end{smallmatrix}$.—7.9 grams of carbethoxyhydroxamic acid were dissolved in water, and neutralized with 4.2 grams of potassium hydroxide. To this solution 10.1 grams (1 mol.)of benzoyl chloride were added. The mixture was shaken until the odor of benzoyl chloride became faint, and a colorless oil had separated. Without removing the oil, the contents of the flask were transferred to a separatory funnel, and extracted with ether. The benzoyl derivative was then extracted from the ether by means of dilute sodium hydroxide, and precipitated from this alkaline solution by means of carbon dioxide. A colorless oil separated, which was again taken up by ether. After drying and evaporating the ether, 8 grams of oil were obtained. After standing for

six months in a desiccator, this oil gave indications of solidifying, and in a few hours became a mass of soft, fibrous crystals, melting at 38°–39°.

0.3104 gram gave 18.6 cc. N_2 at 15° and 744.1 mm.

	Theory for $C_{10}H_{11}NO_4$.	Found.
N	6.69	6.89

Properties.—It can be distilled at diminished pressure, but suffers considerable decomposition; at 180°–190° and 20 mm., a colorless oil passes over, possessing an intense odor of isocyanates, and depositing crystals of benzoic acid on standing. This distillate can be dissolved in alkalies, and reprecipitated by carbon dioxide.

The solid is readily soluble in ether, alcohol, and ligroïn, almost insoluble in water. Alkalies decompose it, even in the cold, on standing for a short time, into benzoic acid, and carbethoxyhydroxamic acid.

Sodium Salt.—By the addition of sodium ethylate to an alcoholic solution of the acid, and precipitation with ether, a white salt is formed. A yellow silver salt separates on adding silver nitrate to a water solution of the sodium salt.

Dibenzoyl Derivative of Carbethoxyhydroxamic Acid,

$$C_2H_5O-C \begin{cases} O-COC_6H_5 \\ N-O.CO.C_6H_5 \end{cases} \text{ or } \begin{matrix} C_2H_5O-C \\ C_6H_5C \end{matrix} \begin{cases} O \\ N-O.COC_6H_5 ? \\ O \end{cases}$$
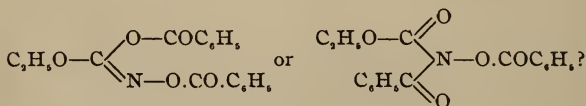
1.5 grams of the sodium salt of the benzoyl ester of carbethoxyhydroxamic acid were suspended in absolute ether, and treated with 0.9 gram of benzoyl chloride; 1.9 grams of oil were obtained on evaporating the ether solution. This solidified partially to a mass of colorless crystals. Recrystallized from ether and ligroïn, it was obtained in transparent, prismatic crystals, melting at 72°–73°.

0.0965 gram gave 0.2301 gram CO_2, and 0.0426 gram H_2O.
0.3275 gram gave 13.4 cc. N_2 at 22° and 743 mm.

	Theory for $C_{17}H_{15}NO_3$.	Found.
C	65.17	65.03
H	4.79	4.90
N	4.47	4.55

Properties.—It is slightly soluble in warm ligroïn, readily soluble in ether, and alcohol.

XVIII.—THE ACTION OF THE HALOGENS ON THE ALIPHATIC AMINES, AND THE PREPARATION OF THEIR PERHALIDES.

By James F. Norris.

In a preliminary communication on the action of the halogens on the methylamines, Remsen and Norris[1] described the preparation and properties of some new compounds formed by the action of iodine on trimethylamine and of bromine on tri- methyl- and dimethylamine. The discovery of the compounds was made in an investigation of some double salts containing selenium and the methylamines, and as their complete study was impossible at that time, a preliminary notice of the re- sults was published. It was shown that a compound of the probable structure $(CH_3)_3N.I_2$ was formed when a solution of iodine in absolute alcohol was treated with dry trimethyl- amine. The addition-product was precipitated as a light yel- low powder, insoluble in water, which rapidly darkened and changed to a viscous liquid after standing a few days. It was decomposed slowly by hot water, and gave up all its iodine when treated with dilute hydrochloric acid, forming tri- methylamine hydrochloride according to the following equa- tion :

$$(CH_3)_3N.I_2 + HCl = (CH_3)_3N.HCl + 2I.$$
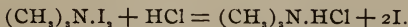
By the action of bromine on dimethyl- and trimethylamine, compounds were formed, which crystallize from a mixture of alcohol and ether in yellow needles. Two possible formulas were considered, $(CH_3)_3N.HBr.Br$ and $(CH_3)_3N.Br_2$. As the trimethylamine compound was prepared at o° from dry tri-

[1] This Journal, 18, 90.

methylamine and bromine which had been freed from hydrobromic acid and water by successive distillation from precipitated manganese dioxide and sulphuric acid, it was concluded that the second formula represented the structure of the compound. The formation of hydrobromic acid by the action of bromine on a methyl group at 0° seemed highly improbable. Further, all the perhalides described up to that time contained two or more added halogen atoms, for example, NH_4I_3, $CsBrI_2$, $CsBr_3$, and $C_6H_5N_2.IBr_2$. The action of bromine was accordingly considered analogous to that of iodine.

These compounds have now been carefully studied, and it has been found that the reactions of the bromides with a number of reagents are not analogous to those of the iodide. It follows, therefore, that they have different structures.

All the reactions of the iodide are in accord with the formula already proposed, $(CH_3)_3N.I_2$. Water does not liberate iodine; dilute acids set free all of the iodine and form the salt of the amine; and concentrated sulphuric acid does not cause an evolution of hydriodic acid, which would be the case if the formula were $(CH_3)_3N.HI.I$. A true periodide, $(CH_3)_3N.HI.I_4$, was treated with concentrated sulphuric acid. Hydriodic acid was set free, thus showing the value of the above test.

The bromide derived from trimethylamine, however, was decomposed by water with liberation of one-half of the bromine. The presence of dilute acids did not affect the decomposition, and concentrated sulphuric acid caused a vigorous evolution of hydrobromic acid. The most probable structure is, therefore, $(CH_3)_3N.HBr.Br$. The correctness of this view was further demonstrated by making the compound from trimethylamine hydrobromide and bromine. Direct addition took place without the formation of hydrobromic acid, thus showing that the hydrogen was not replaced by bromine. If the above structure is correct, bromine readily attacks a methyl group joined to nitrogen, forming hydrobromic acid, for the compound was prepared from pure bromine and pure trimethylamine at 0°. This was shown to be the case by the

following experiments : A cold ethereal solution of bromine, free from hydrobromic acid, was poured into a cold ethereal solution of trimethylamine. As long as the amine was in excess a white precipitate, which proved to be trimethylamine hydrobromide, was formed. On addition of an excess of bromine, the salt changed to a red oil, which proved, on crystallization, to be the bromine addition-product. It follows from this experiment that the hydrobromide is first formed, and from this the dibromide. In a second experiment the dry amine was passed into bromine, kept cool by ice, and the evolved gases passed into water. After the removal of free bromine with precipitated silver from the latter, hydrobromic acid was found. A blank experiment was performed by drawing air through the apparatus in order to test the value of the method. It is, therefore, evident that bromine is readily substituted for hydrogen in a methyl group joined to nitrogen. It has been impossible thus far to isolate the substitution-product formed. The only compound obtained was the perbromide. Pyridine perbromides and periodides of a similar structure have been recently described by Trowbridge and Diehl.[1]

The action of iodine and bromine on a number of aliphatic amines has been studied in order to determine whether the formation of iodine addition-products and perbromides is general. Trimethylamine is the only amine studied which gives a diiodo addition-product. Dimethylamine reacted with iodine dissolved in ether and gave a compound containing two iodine atoms, but its reaction showed that its formula is $(CH_3)_2HN.HI.I$, analogous to the bromides. Diamylamine gave the periodide $(C_5H_{11})_2NH.HI.I_2$. The action of iodine on the amines and their salts is being further investigated.

The reaction between bromine and tricetylamine was studied in order to discover whether the power to form perbromides exists with compounds containing a large number of carbon atoms. No reaction took place. Perbromides were formed from dimethyl, trimethyl, diethyl, triethyl, dipropyl, tripropyl and diamylamines. As the number of carbon atoms increased

the stability of the compounds and their crystallizing power decreased. The propyl and amyl compounds are red oils which crystallize with difficulty and decompose on standing. They all have the structure $R_2N.HBr.Br$, where one R may be hydrogen, and all give off one atom of bromine when dissolved in water. No perbromides of primary amines could be isolated.

By the action of chlorine on trimethylamine a very unstable compound, having the appearance and odor of camphor, was formed. It was impossible to purify or analyze it.

The following perhalides of dimethylamine containing two different halogens have been prepared : $(CH_3)_2NH.HCl.Br$, $(CH_3)_2NH.HCl.I$, $(CH_3)_2NH.HBr.I$. The salts containing two bromine and two iodine atoms are well characterized as stated above, but a number of methods failed to produce the compound containing two chlorine atoms. Analogous compounds containing trimethylamine were prepared. The ease of formation of these perhalides containing two halogens is in accord with the observation of Wheeler[1] that organic compounds form such salts with greater facility than the alkali metals.

Pictet and Krafft[2] have described the compound $(CH_3)_3N.ICl$. Efforts were made to repeat the work as described, but without success. The compound always obtained was the diiodide $(CH_3)_3N.I_2$. By the action of iodine monochloride on trimethylamine the salt $(CH_3)_3N.HCl.I$ was obtained.

Incidentally an improved modification of the method for the preparation of dimethyl- and diethylamine from dimethyl- and diethylaniline is described.

Experimental Part.

WITH E. H. LAWS.

Preparation of Dimethylamine. — A modification of the method of Baeyer and Caro[3] was used, which shortened the process and gave excellent results. 100 grams of nitrosodimethylaniline hydrochloride, prepared as directed by Levy

[1] This JOURNAL, 19, 672. [2] Bull. Soc. Chim. (Paris), [3], 7, 74.
[3] Ber. d. chem. Ges., 7, 964.

(Anleitung zur Darstellung organischer Präparate), was rubbed into a thin paste with warm water and introduced slowly through a funnel with a wide neck into a four-liter flask, provided with a return-condenser, and containing a boiling solution of 90 grams sodium hydroxide dissolved in two liters of water. A glass rod covered with rubber tubing was used as a stopper to close the funnel during the decomposition. The evolved gas was absorbed in hydrochloric acid (sp. gr. 1.12) contained in two Peligot tubes. Almost the theoretical amount of nitrosodimethylaniline hydrochloride is obtained and about a 90 per cent. yield of dimethylamine hydrochloride. About ten hours were required to set up the apparatus and prepare 200 grams of the hydrochloride by this method.

Dimethylammonium Dibromide, $(CH_3)_2NH.HBr.Br.$ —The best method of preparation is as follows: 10 grams of dimethylamine hydrobromide are cautiously treated with 8 grams of bromine. After the cooled solid mass is dried on a porous plate over potassium hydroxide, it is dissolved in cold alcohol, and ether is added until precipitation begins. The solution is cooled with a freezing-mixture when the compound crystallizes in yellow needles. Addition of more ether causes a further precipitation. The salt is very soluble in alcohol, sparingly soluble in hot chloroform and insoluble in ether. It melts at 93° and does not decompose when heated to 200°. When treated with water it melts, forming a heavy red oil, which slowly dissolves. One-half of the bromine is set free, as was shown in a former paper. As the total iodine in the diiodide of trimethylamine was liberated by dilute hydrochloric acid, the amount of halogen set free from the bromide under the same conditions was determined.

0.1498 gram salt gave 0.0587 gram bromine.

Calculated for 1Br.	Found.
38.88	39.23

It is seen, therefore, that the structure of the bromide is not $(CH_3)_2NH.Br_2$. A complete analysis gave the following results:

I. 0.5240 gram salt gave 0.2307 gram CO_2, and 0.1860 gram H_2O.

II. 0.3981 gram salt gave 0.1705 gram CO_2, and 0.1430 gram H_2O.

III. 0.1628 gram salt gave 0.2967 gram AgBr by the Carius method.

IV. 0.4987 gram salt gave 27.7 cc. nitrogen at 0° and 760 mm.

	Calculated for $(CH_3)_2NH.HBr.Br$	I.	II.	III.	IV.
C	11.65	12.00	11.69	....	....
H	3.88	3.98	4.02	....	....
N	6.79	....	....	....	6.77
Br	77.67	....	....	77.56	....

The perbromide was treated with a large excess of bromine in an attempt to prepare a salt containing more halogen atoms. When the excess of bromine was removed by slow evaporation the original salt was obtained. Dry chlorine was passed over a weighed quantity of the perbromide. The loss in weight and analysis of the resulting product showed that but one-half of the bromine was removed, and the formula of the resulting substance was $(CH_3)_2NH.HCl.Br$.

Dimethylammonium Triiodide, $(CH_3)_2NH.HI.I_2$.—An attempt was made to prepare the dimethylammonium diiodide in a manner similar to that used with the dibromide. Dimethylamine hydroiodide in hydriodic acid was treated with iodine. The salt obtained was purified by dissolving in a small amount of ethyl acetate and adding benzene, when it crystallized in long needles with a dark-blue, steely luster. Analysis showed that it was a triiodide.

I. 0.2038 gram salt gave 0.3374 gram AgI.

II. 0.2912 gram salt gave 0.1733 gram free iodine when treated with water.

	Calculated for $(CH_3)_2NH.HI.I_2$	I.	II.
3I	89.20	89.45	....
2I	59.47	....	59.53

The formation of a periodide of dimethylamine has been noted by Schmidt,[1] but no formula is assigned to it. The triiodide melts at 97°, is soluble in alcohol and ether, insoluble

[1] Ann. Chem. (Liebig), **267**, 254.

in chloroform and carbon disulphide. Water decomposes it into the hydroiodide and free iodine, and potassium hydroxide forms iododimethylamine $(CH_3)_2NI$.

Dimethylammonium Diiodide, $(CH_3)_2NH.HI.I$.—The direct addition-product of trimethylamine and iodine is precipitated when the constituents are mixed in alcoholic solution. No precipitate was formed, however, when dimethylamine was used. Evaporation of the solution did not yield a pure product. As the diiodide could not be prepared in this way, an excess of the dry amine was passed into an ethereal solution of iodine. A dark oil separated, which was analyzed after the removal of the ether on a water-bath.

I. 0.3354 gram salt gave 0.5247 gram AgI.
II. 0.3576 gram salt gave 0.5570 gram AgI.

Calculated for $(CH_3)_2NH.HI.I$.	Found.	
	I.	II.
84.65	84.53	84.16

The salt formed was not analogous to the trimethylamine compound, for but one-half of the iodine was liberated in acid solution and hydriodic acid was evolved with concentrated sulphuric acid. It accordingly has the structure $(CH_3)_2NH.HI.I$, similar to that of the bromides.

Dimethylammonium Chloriodides. — Dimethylammonium chloriodide, $(CH_3)_2HN.HCl.I$, was prepared by treating dimethylamine hydrochloride, dissolved in alcohol and chloroform, with iodine, using the constituents in the proportion of one molecule of the former to one atom of the latter. It crystallized slowly in dark-red needles. The substance was analyzed by reducing the iodine set free with sulphur dioxide, and precipitating with silver nitrate. The mixture of silver halides was weighed, then treated with chlorine and weighed again. The results follow:

I. 0.2428 gram salt gave 0.4431 gram AgI + AgCl, which lost 0.1070 gram.
II. 0.2770 gram salt gave 0.5036 gram AgI + AgCl, which lost 0.1212 gram.
III. 0.1502 gram salt gave 0.0926 gram free I.

	Calculated for $(CH_3)_2HN.HCl.I.$	I.	Found. II.	III
Cl	17.01	17.13	17.17	....
I	60.88	61.16	60.72	61.67

The salt melts at 100° and dissolves in water with liberation of all of the iodine. Potassium hydroxide forms iododimethylamine.

When a weighed quantity of this chloriodide was treated with dry chlorine, it melted and the gas was absorbed. After a few hours, during which the salt was gently heated, the increase in weight was equivalent to a molecular quantity of chlorine. The resulting product crystallized from a mixture of alcohol and ether in yellow needles, and gave results on analysis closely approximating the formula $(CH_3)_2NH.HCl.$ $I.Cl_2$.

Dimethylammonium Chlorbromide, $(CH_3)_2NH.HCl.Br.$ — This salt was prepared by the action of bromine on dimethylamine hydrochloride, dissolved in hydrochloric acid, or in chloroform. Addition of carbon disulphide to the chloroform solution causes a precipitation of the compound. It is also formed by the action of chlorine on the perbromide, $(CH_3)_2NH.HBr.Br.$ The analysis resulted as follows:

0.3021 gram salt gave 0.6004 gram AgCl + AgBr, which lost 0.0778 gram when treated with chlorine.

	Calculated for $(CH_3)_2NH.HCl.Br.$	Found.
Cl	21.93	22.22
Br	49.55	46.26

Dimethylammonium Bromiodide, $(CH_3)_2NH.HBr.I.$—This compound was prepared from the bromide and iodine in a manner similar to that used to make the chlorbromide. It is a dark-red, crystalline salt, which melts at 98°–99°.

WITH F. M. SMALLEY.

The work described in this section was done before the correct structure of the substances formed by the action of the halogens on the amines was made clear. Efforts were made to prepare compounds similar to the diiodide of trimethylamine, $(CH_3)_3N.I_2$, by the action of iodine chloride, bromine chloride, and iodine bromide on the free amine. These com-

pounds, however, act like bromine, causing substitution, and forming perhalides. It was found later that the latter could be prepared more advantageously by the method described above for the dimethylamine salts.

Trimethylammonium Chloriodides.—The salt containing two halogen atoms was prepared as follows: A solution of trimethylamine in alcohol was treated with a chloroform solution of iodine monochloride. After standing a few hours in a vacuum-desiccator, the compound crystallized in dark reddish-brown needles, which melt at 84°. With water, iodine was set free. The following analyses were made:

I. 0.1370 gram salt gave 0.2305 gram $AgI + AgCl$, which gave 0.1753 gram $AgCl$.

II. 0.1619 gram salt gave 0.2723 gram $AgI + AgCl$, which gave 0.2064 gram $AgCl$.

	Calculated for $(CH_3)_3N.HCl.I.$	Found.	
		I.	II.
I	57.05	55.91	56.49
Cl	16.00	16.02	15.76

By the action of iodine trichloride on the amine, a second perchloride was obtained. When the substances were mixed in alcoholic solution the temperature rose and a yellow precipitate separated. Before this could be filtered off it dissolved, forming a dark red solution, from which reddish-brown crystals separated on standing, which melted at 84°, and on analysis proved to be the chloriodide, $(CH_3)_3N.HCl.I.$ The preparation was repeated, care being taken to keep the solution cold. The yellow precipitate was removed and dried on a porous plate. It melted at 168°, and on treatment with water it decomposed, liberating chlorine and iodine. The analysis was made as follows: The salt was dissolved in dilute sulphurous acid, the excess of which was removed by gentle heating. An excess of standardized silver nitrate was added; the precipitate filtered off, dried and weighed. The excess of the silver nitrate in the filtrate was titrated with ammonium sulphocyanate. The method gives much better results than the treatment of the mixed silver halides with chlorine or bromine and requires less time. The results follow:

I. 0.3671 gram salt gave 0.8242 gram AgCl + AgI, and required 0.5345 gram Ag for precipitation.

II. 0.3909 gram salt gave 0.8826 gram AgCl + AgI, and required 0.5735 gram Ag for precipitation.

	Calculated for $(CH_3)_3N.HCl.ICl_2$.	Found. I.	II.
Cl	36.40	35.87	36.27
I	43.40	42.95	42.80

Trimethylammonium Chlorbromide, $(CH_3)_3N.HCl.Br$.—This compound was prepared by the action of chlorine on the dibromide, and of bromine on the hydrochloride dissolved in hydrochloric acid. It crystallizes in yellow needles and dissolves in water with evolution of bromine. The analysis gave figures approximating the above formula.

Trimethylammonium Bromiodide, $(CH_3)_3N.HBr.I$.—To a chloroform solution of iodine bromide was added an alcoholic solution of trimethylamine. After standing in a vacuum-desiccator for a number of days a mixture of white and red crystals appeared. The former proved to be the trimethylamine hydrobromide, and the latter the bromiodide. This salt crystallizes in maroon needles, melts at 89°, and gives up iodine when acted upon by water. The analyses follow :

I. 0.4501 gram salt gave 0.7113 gram AgI + AgBr, and required 0.3624 gram Ag for precipitation.

II. 0.4557 gram salt gave 0.7338 gram AgI + AgBr, and required 0.3745 gram Ag for precipitation.

	Calculated for $(CH_3)_3N.HBr.I$.	Found. I.	II.
Br	30.00	29.35	28.97
I	47.50	48.11	48.50

Action of Chlorine on Trimethylamine.—Dry chlorine and dry trimethylamine react, forming a very hygroscopic substance, which evolves chlorine in the air. The two gases were passed into absolute ether, which was well cooled. A heavy white precipitate formed, which decomposed spontaneously when the ether was removed. It was impossible to determine the composition of the substance.

WITH A. E. KIMBERLY.

Preparation of Diethylamine.—The method of Kopp[1] for

[1] Ber. d. chem. Ges., **8**, 621.

the preparation of diethylamine was much shortened by proceeding as follows: A solution of 50 grams of diethylaniline in 148 grams of hydrochloric acid (sp. gr. 1.12) diluted with 75 cc. water, was diazotized with 32 grams of sodium nitrite, dissolved in 50 cc. of water. The nitrite was added to the solution cooled by ice and salt. After standing a few minutes the solution of nitrosodiethylaniline hydrochloride was slowly run into a four-liter flask provided with a condenser, and containing a boiling solution of 85 grams of sodium hydroxide dissolved in two liters of water. The solution of diethylamine which distilled over was collected in dilute hydrochloric acid. The contents of the flask were boiled for three-quarters of an hour after all the nitroso compound had been introduced. A yield of 75 per cent. of diethylamine was obtained after rectification.

Diethylammonium Dibromide, $(C_2H_5)_2NH.HBr.Br.$[1]—This salt was prepared by adding an ethereal solution of the amine to an ethereal solution of bromine. Also by the action of bromine on the hydrobromide. It crystallizes in reddish-yellow needles, and when treated with potassium hydroxide yielded a heavy yellow, insoluble oil, which is being further investigated. The following analysis was made:

0.2071 gram salt gave 0.3220 gram AgBr.

	Calculated for $(C_2H_5)_2NH.HBr.Br.$	Found.
Br	68.33	68.22

Experiments with Triethylamine. — Triethylamine was treated with bromine, both in ethereal solution. When there was an excess of the amine the hydrobromide was formed. An excess of bromine caused the separation of an oil which did not solidify after standing three weeks. It could not be purified from the excess of bromine without decomposition. The hydrobromide of the amine was treated with bromine in the way used in the preparation of the perbromide of dimethylamine. A red oil resulted, which could not be purified. Evidently the perbromide, if formed, was very unstable.

[1] This salt, as well as the dibromide from diamylamine was prepared and analyzed by L. L. Lamborn.

Dipropylammonium Dibromide, $(C_3H_7)_2NH.HBr.Br.$—This compound was prepared in the usual way from the hydrobromide and bromine. The resulting oil on long standing crystallized. It was purified by dissolving in alcohol and adding ether. Reddish-yellow crystals separated when the solution was cooled by ice and salt. In properties it resembles the other perbromides, but is much stable, as shown by the analysis. The sample used had no odor of bromine.

0.1995 gram salt gave 0.2507 gram AgBr.

	Calculated for $(C_3H_7)_2.NH.HBr.Br.$	Found.
Br	61.01	55.21

When treated with sodium hydroxide the perbromide gives a yellow oil with a strong odor.

Tripropylammonium Dibromide, $(C_3H_7)_3N.HBr.Br.$ — The method used in the preparation of the dipropyl compound was followed here. The body readily loses bromine. Analysis of crystals washed free from bromine with petroleum ether gave the following results :

0.2138 gram salt gave 0.2600 gram AgBr.

	Calculated for $(C_3H_7)_3N.HBr.Br.$	Found.
Br	54.98	52.00

Diamylammonium Dibromide, $(C_5H_{11})_2NH.HBr.Br.$ — Diamylamine and bromine in ethereal solution gave a red oil, which after washing with ether was analyzed.

0.3061 gram salt gave 0.3536 gram AgBr.

	Calculated for $(C_5H_{11})_2NH.HBr.Br.$	Found.
Br	50.31	49.18

Experiments with Tricetylamine.—Tricetylamine, prepared according to Fridau's[1] directions, was dissolved in ether and treated with bromine. As no precipitate was formed the ether was evaporated, when a dark oil appeared, which solidified to a white mass after it was washed free from bromine. After drying, it melted at 38°–40° and contained no bromine. Tricetylamine melts at 39°. It is evident, therefore,

[1] Ann. Chem. (Liebig), **83,** 25.

that the power to form perbromides exists only with the amines containing a small number of carbon atoms.

Investigation of the Structure of the Compounds.—Trimethylamine diiodide, $(CH_3)_3N.I_2$, was prepared according to the directions already given. It was treated with dilute hydrochloric acid, and the iodine set free titrated with sodium thiosulphate. All of the iodine in the compound was liberated. Another portion was treated with concentrated sulphuric acid. There was a separation of iodine, but no hydriodic acid was formed, whereas the gas was easily recognized when a perhalide, $(CH_3)_3N.HI.I_4$, was acted on by sulphuric acid.

The dibromide was studied in the same way. Dilute hydrochloric acid did not affect the decomposition with water, which liberated one-half of the bromine, and concentrated sulphuric acid caused a vigorous evolution of hydrobromic acid. Three grams of trimethylamine hydrobromide were treated in a dry flask with pure bromine. Air was drawn through the flask and then through water. When the reaction was complete the latter was shaken with precipitated silver, filtered, and titrated with tenth-normal sodium hydroxide. 0.3 cc. of the alkali was used, thus showing that no hydrobromic acid was evolved, and that the compound was formed by the direct addition of bromine to the hydrobromide.

The salt was also prepared by the action of pure bromine on pure trimethylamine, both dissolved in ether, and in absence of a solvent. The formula $(CH_3)_3N.HBr.Br$ requires hydrobromic acid. The following experiment showed that the hydrogen necessary was furnished by the amine. To a cold solution of trimethylamine in ether, was added a cold solution of pure bromine in ether. As long as the amine was in excess a white precipitate was formed. This on analysis proved to be trimethylamine hydrobromide. The other product of reaction could not be isolated. Carefully dried trimethylamine was passed into bromine cooled by ice-water. The evolved gas was drawn through water which, after the removal of free bromine, was titrated with a standard alkali. A blank determination was made by drawing air through the apparatus. In both cases the experiment was continued for

an hour. Acid equivalent to 1.5 cc. tenth-normal sodium hydroxide was obtained with the blank, whereas 14 cc. were required for neutralization when the amine was used. It follows that more hydrobromic acid than is necessary to unite with all the amine is formed by the direct action of bromine.

Attempts to Prepare the Compound $(CH_3)_3N.ICl$.—Pictet and Krafft[1] have described a compound of the above formula which is analogous to the diiodide prepared by us, $(CH_3)_3N.I_2$. As the chloriodine addition-product was not obtained by the direct action of iodine monochloride on trimethylamine, efforts were made to obtain it according to Pictet and Krafft. The directions given were followed, but without success. By the action of iodine trichloride on trimethylamine, they obtained a compound of the formula $(CH_3)_3N.HCl.ICl$, which crystallized in yellow leaflets and melted at 159°. When this was treated with sodium carbonate the addition-product $(CH_3)_3N.ICl$ was formed as a precipitate, which crystallized from ether. The yellow salt was formed as described, but treatment of a solution of it with sodium carbonate, under a variety of conditions, yielded only the diiodide, $(CH_3)_3N.I_2$.

BOSTON, MASS., November 1, 1897.

LV.—ON ACYL IMIDO ESTERS.

SECOND PAPER.

BY H. L. WHEELER, P. T. WALDEN, AND H. F. METCALF.

In a previous paper, by two of us, it was shown that the imidomethyl and ethyl benzoates give acyl derivatives with acetyl and benzoyl chloride, the reaction taking place as follows:

$$2C_6H_5C \begin{matrix} \diagup NH \\ \diagdown OCH_3 \end{matrix} + ClCOCH_3 = C_6H_5C \begin{matrix} \diagup NCOCH_3 \\ \diagdown OCH_3 \end{matrix} +$$

$$C_6H_5C \begin{matrix} \diagup NH_2 \\ -Cl \\ \diagdown OCH_3 \end{matrix} .$$
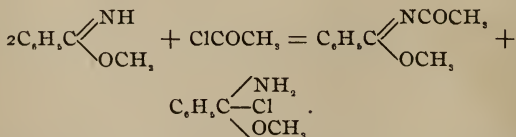
Two molecules of the imido ester react with one molecule of

[1] Bull. Soc. Chim. [Paris], [3], **7**, 74.

acyl chloride, giving one molecule of acylimido ester and one molecule of the imido ester hydrochloride.

We now find that the acylimido esters may also be prepared from the silver salts of diacyl amides. Silver dibenzamide gave, with ethyl iodide, a product identical in every respect with that obtained from benzimidoethyl ester and benzoyl chloride; *i. e.*, $C_6H_5C\overset{\displaystyle NCOC_6H_5}{\underset{\displaystyle OC_2H_5}{\big<}}$. The product had entirely different properties from those of the isomeric nitrogen ethyl compound, $C_6H_5CON(C_2H_5)COC_6H_5$, which was prepared from ethylbenzamide. The reaction, therefore, takes place as follows:

$$C_6H_5C\overset{\displaystyle NCOC_6H_5}{\underset{\displaystyle OAg}{\big<}} + IC_2H_5 = C_6H_5C\overset{\displaystyle NCOC_6H_5}{\underset{\displaystyle OC_2H_5}{\big<}} + AgI.$$
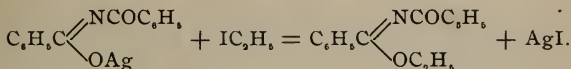
The behavior of the silver salts of diacyl amides towards ethyl iodide is thus shown to be perfectly analogous to that of the silver salts of monoacylamides[1] and anilides.[2]

The acylimido esters are very reactive substances, and it was with difficulty that some were obtained in a state of approximate purity. They react with water, immediately in the presence of acids, in either of two ways; *i. e.*, alcohol is separated, and a diacylamide results, or a monoacylamide and an ester are formed. These decompositions may be represented as follows:

$$C_6H_5C\overset{\displaystyle NCOC_6H_5}{\underset{\displaystyle OCH_3}{\big<}} + H_2O = C_6H_5C\overset{\displaystyle\overset{\displaystyle N\overset{\displaystyle COC_6H_5}{\underset{\displaystyle H}{\big<}}}{\big|}}{\underset{\displaystyle OCH_3}{\overset{\displaystyle O H}{\big|}}}$$
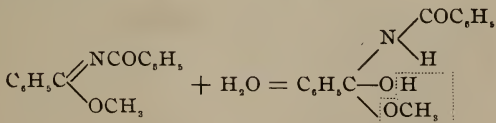
As far as observed, the acetyl, propionyl, butyryl, carbethoxyl, and benzoylbenzimido esters behave in the above manner, while benzoylphenylacetimidoethyl ester and those imido esters containing the acyl group, $-COCO.OC_2H_5$, do not give diacyl amides, but readily decompose as follows:

[1] Tafel and Enoch: Ber. d. chem. Ges., **23**, 104.

[2] Comstock and Kleeburg: *Ibid*, **12**, 493.

$$C_6H_5CH_2C \big\langle^{NCOC_6H_5}_{OC_2H_5} + H_2O = C_6H_5CH_2C - O \vert H \; \underset{OC_2H_5}{\overset{N\big\langle^{COC_6H_5}_{H}}{\big\vert}}$$
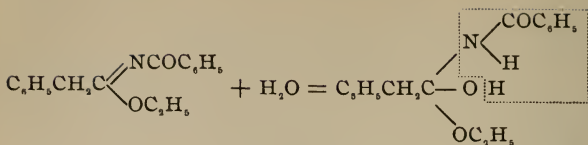
These reactions show conclusively that the diacyl amides have both acyl groups attached to nitrogen.

To what extent the acylimido esters decompose according to the first representation, otherwise than indicated above, remains to be investigated. At present this decomposition suggests an easy method for the preparation of certain diacyl amides, it being only necessary to treat the reaction-product of an acyl chloride and an imido ester, with hydrochloric acid, when the diacyl amide immediately separates pure and in crystalline form.

The instability of the acylimido esters in the presence of moisture, acids, etc., recalls the similar behavior of the oxygen ethers of succinimide,[1] which readily separate alcohol and revert to succinimide. The grouping $RC \big\langle^{NR'}_{OC_2H_5}$ becomes less stable in the presence of moisture as the negative character of the groups R and R' are increased.

When benzoylbenzimidoethyl ester is heated with benzoyl chloride it reacts slowly and tribenzamide results :

$$C_6H_5C \big\langle^{NCOC_6H_5}_{OC_2H_5} + ClCOC_6H_5 = C_6H_5C - \underset{OC_2H_5}{\overset{N\big\langle^{COC_6H_5}_{COC_6H_5}}{\big\vert}} Cl$$
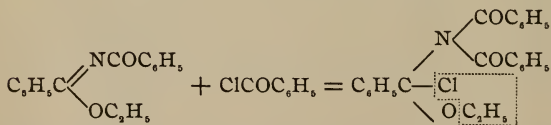
This reaction is analogous to the action of acyl chlorides on the isoanilides,[2] in which case diacylanilides were formed. It therefore indicates that in the triacylamides all three acyl groups are attached to nitrogen. An attempt was made to determine the structure of the triacylamides and to prove the

[1] Comstock and Wheeler : This JOURNAL, **13**, 519.
[2] Wheeler and Walden : This JOURNAL, **19**, 129.

equivalence of the three bonds of nitrogen, in respect to acyl groups, by allowing benzoyl chloride to react on acetylbenzimidoethyl ester, on the one hand, and acetyl chloride on benzoylbenzimidopropyl ester on the other. Tribenzamide, however, was formed in the first case while, in the second, nothing but decomposition-products were observed.

When the acylimido esters are treated with ammonia or bases, acylamidines are formed :

$$C_6H_5C\underset{OC_2H_5}{\overset{NCOC_6H_5}{<}} + H_2NR = C_6H_5C\underset{NHR}{\overset{N\underset{H}{\overset{COC_6H_5}{<}}}{-}}OC_2H_5 \;\; .$$
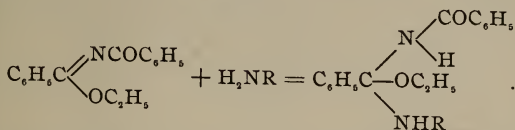
The structure of these cannot be determined by their method of formation since the above hypothetical addition-product can give up alcohol in two ways, giving either

$$C_6H_5C\underset{NHR}{\overset{NCOC_6H_5}{<}} \quad \text{or} \quad C_6H_5C\underset{NR}{\overset{NHCOC_6H_5}{<}} \;\; .$$
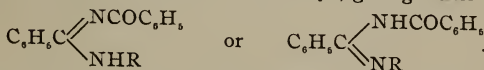
The acylamidines will be described in a later paper.

When benzoylbenzimidoethyl ester was heated in a stream of dry ammonia the following decomposition was observed :

$$C H_6C\underset{OC_2H_5}{\overset{N\,COC_6H_5}{<}} = C_6H_5CN + (C_6H_5CN)_3 + C_6H_5CONH_2 + C_2H_5OH.$$
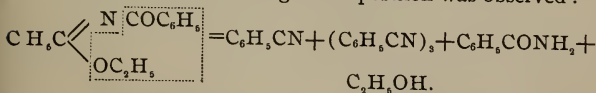
The violence with which acyl chlorides, but especially acetyl chloride, react with the imido esters, isoanilides, or compounds containing the arrangement $RC\underset{OR''}{\overset{NR'}{<}}$, in which the radical R' is not a negative (acyl) group, suggests that it would be of interest to compare the behavior of some rings supposed to contain this grouping. At present we have tried the trimethyl ester of normal cyanuric acid. This, if constituted as described in the text-books, formula (A), contains three of the above groups and should react, giving the triacetyltricarbonimide of Ponomarew.[1]

[1] Ber. d. chem. Ges., 18, 3275.

$$\begin{array}{ccc}
 & N & \\
 & \diagup \; \diagdown\!\!\diagdown & \\
CH_3O{-}C & & C{-}OCH_3 \\
\| & & | \\
N & & N \\
\diagdown & & \diagup\!\!\diagup \\
 & C{-}OCH_3 & \\
 & (A). &
\end{array}
\qquad
\begin{array}{ccc}
 & N & \\
 & \diagup \; | \; \diagdown & \\
CH_3OC & & COCH_3 \\
| & & | \\
N\diagdown & & \diagup N \\
 & \diagdown | \diagup & \\
 & COCH_3 & \\
 & (B). &
\end{array}$$
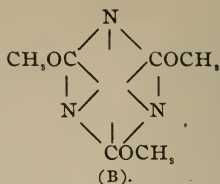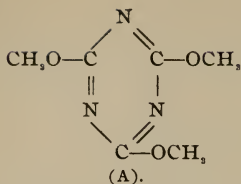
The trimethyl ester was prepared by the directions of Hofmann[1] from cyanuric chloride and sodium methylate. It was then found that this ester can be crystallized unaltered from acetyl chloride, and no action at the boiling-point of acetyl chloride was observed. It seems, therefore, improbable that there are three double unions in the normal cyanuric esters, or, which is practically the same, that they contain para bonds. The inertness of this ester, however, might be explained by the centric formula (B), or it may be due to the ring formation. It is our intention to continue this work on the action of acyl chlorides on ring-formed compounds which, theoretically, may be considered as derived from the grouping RC⟨$^{NR'}_{OR''}$.
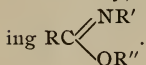
Experimental Part.

Benzimidomethyl Ester, $C_6H_5C\diagup^{NH}_{\diagdown OCH_3}$.—For the preparation of acylimido esters, freshly prepared and distilled imido esters were used. The imido ester hydrochlorides were prepared by Pinner's well-known method, and the free esters according to Bushong's directions.[2]

This compound boiled at 96° under a pressure of 13 mm. Bushong found it to boil at 96° at 10 mm. In a previous paper[3] it was stated that benzimidomethyl ester deposits benzamide on standing. This is not the case when the ester is prepared from benzonitrile by the method of Pinner, and then distilled. The pure ester may be kept for months without

[1] Ber. d. chem. Ges., **19**, 2063.　　　[2] This JOURNAL, **18**, 490.
[3] This JOURNAL, **17**, 398.

any apparent change. A specimen exposed in a test-tube plugged with cotton, after standing a year, deposited a few crystals. These melted at 230°, and were, therefore, cyanphenine.

The Picrate, $C_6H_5C\begin{smallmatrix}NH\\OCH_3\end{smallmatrix}.C_6H_2(NO_2)_3.OH$.—An alcoholic

solution of picric acid added to benzimidomethyl ester in ether gives a heavy, lemon-yellow, crystalline precipitate. This melts at 163° and from alcohol or water it forms stout prisms. A nitrogen determination gave:

	Calculated for $C_{14}H_{12}N_4O_8$.	Found.
N	15.38	15.06

Benzoylbenzimidomethyl Ester, $C_6H_5C\begin{smallmatrix}NCOC_6H_5\\OCH_3\end{smallmatrix}$. — When

benzoyl chloride is mixed with benzimidomethyl ester in ethereal solution, in the proportion of one molecule of the former to two of the latter the reaction is practically complete in twenty-four hours. It was found advisable to treat the reaction-product here, as in most of the other cases, as follows: On filtering from the imido ester hydrochloride, the ether solution was shaken with dilute alkali, dried over solid potassium hydrate, then calcium chloride, and finally, on evaporating off the ether, the products were usually obtained as oils. This compound, unlike the corresponding ethyl and isobutyl derivatives, refused to solidify without decomposition. It was found to boil from 210° to 212° at 12 mm. pressure. A nitrogen determination in the colorless oil thus obtained gave:

	Calculated for $C_{15}H_{13}NO_2$.	Found.
N	5.8	5.5

When benzoylbenzimidomethyl ester is treated with a drop of hydrochloric acid in alcoholic solution, dibenzamide separates. Dibenzamide is also deposited when the material is allowed to stand.

Carbethoxylbenzimidomethyl Ester, $C_6H_5C\begin{smallmatrix}NCO_2C_2H_5\\OCH_3\end{smallmatrix}$. —

Benzimidomethyl ester and chlorcarbonic ethyl ester were boiled in ethereal solution for a number of hours. On cooling the ethereal solution, plates separated. These melted at about 126° and on crystallizing from water melted at 128°. This material proved to be benzamide. The ether was evaporated, and a mixture of oil and crystals of benzamide obtained; on distilling this at 14 mm. it was found to boil from 148° to 156°. This fraction was treated with a mixture of equal volumes of ether and ligroïn, filtered from precipitated benzamide, and then, after evaporating the solvent, a colorless oil was obtained which boiled at 155° at 14 mm. pressure. A nitrogen determination gave the following result :

	Calculated for $C_{11}H_{13}NO_3$.	Found.
N	6.7	6.9

Benzoylurethane, $C_6H_5CONHCO_2C_2H_5$.—A few drops of the above material were treated with cold dilute hydrochloric acid, the mass then solidified and, on washing with water, it melted from 110°–111°. This solid dissolved readily in dilute sodium hydroxide, and was precipitated unaltered by dilute hydrochloric acid. It had all the properties of benzoylurethane, as described by Pechmann.[1]

Ethyloxalylbenzimidomethyl Ester, $C_6H_5C\begin{smallmatrix}\diagup NCOCO_2C_2H_5\\\diagdown OCH_3\end{smallmatrix}$.—

7.7 grams of ethyl chloroxalate were slowly dropped into 15.4 grams of benzimidomethyl ester, largely diluted with dry ether. The reaction is violent and is complete when the ester is all added. On filtering and evaporating the ether a clear colorless oil was obtained. This was distilled at 23 mm. pressure. Below 206° a few drops collected, the latter portion of which solidified in flattened prisms, which melted at 114°–115° and proved to be oxamethane. From 206°–207° a thick syrup distilled over, which constituted almost the entire portion. It was redistilled at 14 mm., when it boiled at 192°. The latter portion of this distillate gave on analysis :

	Calculated for $C_{12}H_{13}NO_4$.	Found.
N	5.95	6.21

[1] Ber. d. chem. Ges., **28**, 2383.

When ethyl oxalylbenzimidomethyl ester is exposed to the air for some time, or when boiled with water, the odor of benzoic ester is noticed and oxamethane results. The formation of benzoyloxamethane was not observed in this case, the decomposition taking place according to the second method mentioned in the introduction. Concentrated aqueous ammonia immediately decomposes this acylimido ester into oxamide and methyl benzoate. It soon solidifies when mixed with aniline.

Benzimidoethyl Ester, $C_6H_5C\overset{\diagup NH}{\underset{\diagdown OC_2H_5}{}}$.—This was prepared by the method of Pinner. It was observed to distil at 101°–102° at 15 mm. pressure. Bushong[1] gives its boiling-point as 106°–109° at 15 mm.

Benzimidoethylester Mercuric Chloride, $C_6H_5C\overset{\diagup NH.HgCl}{\underset{\diagdown OC_2H_6}{-Cl}}$.— Not only do the imido esters give well-crystallized addition-products with picric acid, but also in some cases with mercuric chloride. The above was prepared by adding benzimidoethyl ester to an alcoholic solution of mercuric chloride. The addition-product then separates in a mass of colorless needles. It was recrystallized from ether, and a chlorine determination gave the following result :

	Calculated for $C_9H_{11}NOHgCl_2$.	Found.
Cl	16.9	16.9

Acetylbenzimidoethyl Ester, $C_6H_5C\overset{\diagup NCOCH_3}{\underset{\diagdown OC_2H_6}{}}$.—This compound we described in a previous paper. We have now prepared it in larger quantities, and find its boiling-point to be 156° at 17 mm. instead of 151°.

When acetylbenzimidoethyl ester is mixed with benzoyl chloride, and the mixture kept at a temperature of 100°–120° for a number of hours, a mass of needles separates. This proved to be tribenzamide.

[1] *Loc. cit.*

Propionylbenzimidoethyl Ester, $C_6H_5C\begin{array}{c}NCOC_2H_5\\OC_2H_5\end{array}$.—The mixture in this case was allowed to stand for twenty-four hours, and then treated as in the case of benzoylbenzimido-methyl ester. The product was an oil which, on fractioning, boiled between 161° and 162° at 17 mm. pressure. A nitrogen determination gave :

	Calculated for $C_{12}H_{15}NO_2$.	Found.
N	6.83	7.08

Propionylbenzamide, $CH_3CH_2CO.NHCOC_6H_5$.—When the ethereal solution of propionylbenzimidoethyl ester is shaken with a few drops of concentrated hydrochloric acid, and the ether evaporated, this diacyl amide separates in the form of needles or prisms. Crystallized from alcohol it melts at 98°. A nitrogen determination gave :

	Calculated for $C_{10}H_{11}NO_2$.	Found.
N	7.91	8.08

Normal Butyrylbenzimidoethyl Ester, $C_6H_5C\begin{array}{c}NCOC_3H_7\\OC_2H_5\end{array}$.— Normal butyryl chloride produces an immediate precipitate when added to benzimidoethyl ester dissolved in ether. The mixture was allowed to stand twenty-four hours, and then treated as in the case of benzoylbenzimidomethyl ester. The product was an oil which, on fractioning, boiled at 167° at 16 mm. pressure. A nitrogen determination gave :

	Calculated for $C_{13}H_{17}NO_2$.	Found.
N	6.39	6.64

Normal Butyrylbenzamide, $C_3H_7CO.NH.COC_6H_5$. — On shaking the ethereal solution of the above acylimido ester with concentrated hydrochloric acid, this compound separates in the form of beautiful colorless prisms. These, after three crystallizations from alcohol, melted constantly at 104°–105°. A nitrogen determination gave :

	Calculated for $C_{11}H_{13}NO_2$.	Found.
N	7.33	7.96

Benzoylbenzimidoethyl Ester, $C_6H_5C \underset{OC_2H_5}{\overset{NCOC_6H_5}{<}}$.—This acyl-imido ester is the easiest to obtain in the solid condition, and therefore probably purer than the corresponding benzoylbenzimidomethyl and propyl esters, which were obtained only in the form of oils. In addition to the method already given, this compound was prepared from silver dibenzamide, as follows: 12 grams of the silver salt, dried at 100°, were suspended in ether and boiled with an excess of ethyl iodide. After several hours the ether, on evaporation, gave an oil, which soon solidified, giving the characteristic lozenge-shaped crystals melting at 65°. Sulphuric acid converted the material into dibenzamide.

Tribenzamide, $(C_6H_5CO)_3N$.—4.0 grams of the above compound were heated with 2.2 grams of benzoyl chloride. Little or no reaction took place below 100°, even at 130°–150° the evolution of gas (ethyl chloride) was slow. After several hours crystals were obtained. These, when crystallized from alcohol, melted at about 202°, and were, therefore, tribenzamide. A nitrogen determination gave:

	Calculated for $C_{21}H_{15}NO_3$.	Found.
N	4.25	4.39

Ethyldibenzamide, $(C_6H_5CO)_2NC_2H_5$.—For the preparation of this compound, which is isomeric with benzoylbenzimidoethyl ester, we wish to express our thanks to Mr. T. E. Smith. He prepared this amide as follows: Ethylbenzamide was prepared by the Baumann-Schotten method. The sodium salt of this, suspended in toluene with benzoic anhydride, gave ethyldibenzamide. The product thus obtained crystallized from alcohol in colorless prisms, melting at 101°–102°. A nitrogen determination gave:

	Calculated for $C_{16}H_{15}NO_2$.	Found.
N	4.9	5.2

Ethyloxalylbenzimidoethyl Ester, $C_6H_5C \underset{OC_2H_5}{\overset{NCOCO_2C_2H_5}{<}}$.—

Ethyl chloroxalate reacts violently when mixed with benz-
imidoethyl ester dissolved in ether. The product is an oil
which, on fractioning, boils from 190°–195° at 11 mm. pres-
sure. The crude material generally contains oxamethane
which distils over in the first portions. An analysis of the
above fraction gave the following result:

	Calculated for $C_{13}H_{15}NO_4$.	Found.
N	5.8	6.0

This material readily decomposes into oxamethane and
ethyl benzoate. The formation of benzoyloxamethane was
not observed.
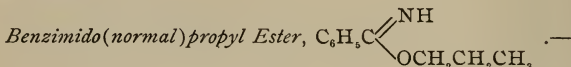
Benzimido(normal)propyl Ester, $C_6H_5C\begin{smallmatrix}\diagup NH \\ \diagdown OCH_2CH_2CH_3\end{smallmatrix}$.—
Pinner does not mention this imido ester in his work "Die
Imidoaether und ihre Derivate." We obtained it as a color-
less, pleasant-smelling oil, which boiled unaltered at 115.5° at
12 mm. pressure, and at 232° at 765 mm. pressure.

	Calculated for $C_{10}H_{13}NO$.	Found.
N	8.59	8.59

The hydrochloride melts at 125°, giving off ethyl chloride
and forming benzamide.

	Calculated for $C_{10}H_{13}NO.HCl$.	Found.
Cl	17.79	17.77

The picrate, obtained in the same manner as the corre-
sponding methyl ester derivative, forms lemon-yellow prisms,
which melt with charring at 261°, or 98° higher than the picrate
of benzimidomethyl ester.
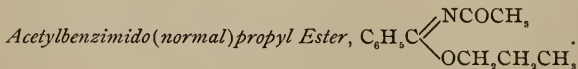
Acetylbenzimido(normal)propyl Ester, $C_6H_5C\begin{smallmatrix}\diagup NCOCH_3 \\ \diagdown OCH_2CH_2CH_3\end{smallmatrix}$.
—When acetyl chloride is added to the imido ester in ether
the separation of hydrochloride begins at once. The mixture
was allowed to stand twelve hours, the ether solution was shaken
with dilute sodium hydrate, and, on drying and evaporating,
an oil was obtained. This was distilled at 12 mm. pressure,

and the fraction boiling from 153°–160° was redistilled, when the main portion boiled at 153° at 13 mm. pressure. A nitrogen determination gave:

	Calculated for $C_{12}H_{15}NO_2$.	Found.
N	6.83	6.79

When this acyl imido ester is exposed to the air or treated with acids it deposits acetbenzamide.

Benzoylbenzimido (normal) propyl Ester, $C_6H_5C\diagup_{OCH_2CH_2CH_3}^{NCOC_6H_5}$.

This compound was obtained in the form of an oil which was distilled at 17 mm. pressure; the portion boiling from 231°–232.5° was analyzed with the following result:

	Calculated for $C_{17}H_{17}NO_2$.	Found.
N	5.24	5.20

When treated with dilute hydrochloric acid it gave dibenzamide.

Benzimidoisobutyl Ester, $C_6H_5C\diagup_{OC_4H_9}^{NH}$.—Pinner found that when this imido ester is liberated from the hydrochloric acid salt, by means of ammonia, and then a distillation is attempted, it is largely decomposed. We have found that if it is liberated by means of a ten per cent. solution of ice-cold sodium hydroxide, and then distilled under diminished pressure, it can afterwards be distilled at ordinary pressures without the slightest decomposition. It was observed to boil at 9 mm. pressure at 117°.5 to 120°, and at ordinary pressure from 248°–250°. It gives an oily precipitate with alcoholic mercuric chloride, which finally solidifies.

Benzoylbenzimidoisobutyl Ester, $C_6H_5C\diagup_{OC_4H_9}^{NCOC_6H_5}$. — The product in this case was an oil which, when distilled at 15 mm. pressure, boiled from 228°–235°. The distillate easily solidified and, on crystallizing from ligroïn, it melted constantly at 54.5".

	Calculated for $C_{18}H_{19}NO_2$.	Found.
N	4.9	4.9

Phenylacetimidomethyl Ester, $C_6H_5CH_2C\begin{smallmatrix}\nearrow NH \\ \searrow OCH_3\end{smallmatrix}$.–The hydro-

chloride of this imido ester was prepared by Pinner. He does not mention the free base. When prepared as stated in the case of benzimidoisobutyl ester, it gave a pleasant-smelling oil, which distilled at 114.5°–115° at 20 mm. pressure.

Phenylacetimidoethyl Ester, $C_6H_5CH_2C\begin{smallmatrix}\nearrow NH \\ \searrow OC_2H_5\end{smallmatrix}$. — It was

found that this ester could be distilled under diminished pressure. It boiled at 116° at 15 mm. pressure. On attempting then to distil it at ordinary pressure it decomposed into alcohol and the nitrile.

Benzoylphenylacetimidoethyl Ester, $C_6H_5CH_2C\begin{smallmatrix}\nearrow NCOC_6H_5 \\ \searrow OC_2H_5\end{smallmatrix}$.

—This was obtained as an oil which did not solidify without decomposition. It boils from 215°–216° at 13 mm. pressure.

	Calculated for $C_{17}H_{17}NO_2$.		Found.
N	5.2		5.9

In one attempt to prepare the above, a mass of plates separated on evaporating the ether solution. These melted at 128° and contained 11.31 per cent. nitrogen; calculated for benzamide, 11.56. The compound, therefore, readily decomposes into benzamide and phenyl ethyl acetate. The above analyzed material evidently contained some benzamide, which explains the high result for nitrogen.

NEW HAVEN, November, 1897.

LVI.—NOTE ON DOUBLE SALTS OF THE ANILIDES WITH CUPROUS CHLORIDE AND CUPROUS BROMIDE.

By WILLIAM J. COMSTOCK.

In studying the behavior of certain "Schiff bases" toward cuprous chloride and cuprous bromide, it seemed to me desirable to find derivatives of the cuprous halides which should be soluble in organic solvents and give up the halides easily. In looking for such derivatives, I found the acetanilide salts here described. As the anilides enter so few combinations in which the basic character of the nitrogen appears, it seems worth while to show that acetanilide is not an exceptional case. The formyl compounds give similar double salts with the greatest ease, but the formyl group splits off so easily under the condition necessary for their formation, that accurate analytical results are difficult to obtain. For instance, when formanilide is added to a solution of cuprous bromide in a mixture of formic and hydrobromic acids, there is formed at once a salt crystallizing beautifully in well-developed, colorless, doubly-terminated prisms. On standing for but a few minutes at ordinary temperature, a change into small plates with very noticeable pearly luster, can be observed. These plates consist of the double salt of aniline with cuprous bromide, $C_6H_5NH_2HBrCuBr$. The corresponding salt of form-paratoluide was, however, obtained, and gave on analysis sufficiently accurate results.

An interesting series of perhalides of the anilides has been carefully studied in this laboratory by Wheeler and Walden.[1] It will be seen that the salts here described,

$$(Anilide)_2 + HBr + CuBr, \text{ and } (anilide)_2 + HBr + 2CuBr,$$

correspond to two of the three types of perhalides obtained by the above-mentioned investigators.

Experimental.

$(C_6H_5NH.COCH_3)_2HClCuCl.$—An advantageous solution for the preparation of this salt consists of a mixture of one

[1] This JOURNAL, 18, 85.

volume of glacial acetic acid, one volume of strong hydro-
chloric acid, and two volumes of water. The acetanilide and
cuprous chloride are dissolved in the hot mixture in the pro-
portion indicated in the above formula. On cooling, the so-
lution solidifies to a mass of long, thin, white prisms. When
freshly prepared and not quite dry, the salt dissolves easily in
alcohol, crystallizing in beautiful, long prisms, when the hot
concentrated solution is allowed to cool slowly. This com-
plete solution in alcohol is doubtless due to the small quantity
of hydrochloric acid which has not yet been removed, as the
perfectly dry salt always leaves a small residue of cuprous
chloride when treated with alcohol. However, many grams
of the dried substance will form a clear solution in alcohol to
which a few drops of dilute hydrochloric acid are added.
Methyl alcohol and acetone can also be used for recrystalliz-
ing it. Protracted boiling of the solution splits off the acetyl
group. The compound has no sharp melting-point. When
heated slowly it darkens at about 140°; complete fusion, ac-
companied by violent decomposition, takes place near 170°.
Freshly prepared it is entirely colorless, but it usually has a
faint yellow color by the time it is dry, especially when pre-
pared in quantity. When dry it is quite stable, and can be
kept for months with no change of color, unless exposed to
moist air. It does not lose hydrochloric acid *in vacuo* over
potassium hydroxide, and when dry can be heated to 100°
without loss of weight. The following analytical results were
obtained :

	Calculated for above composition.	I.	II.
		Found.	
Cu	15.64	15.73	15.77
Cl	17.51	17.50	17.47

$(C_6H_5NHCOCH_3)_2HBr.CuBr.$—This salt can be prepared
from its constituents by using a mixture of one volume glacial
acetic acid, one volume hydrobromic acid (sp. gr. 1.49), and
two volumes of water. More advantageous, however, is the
preparation in alcoholic solution. The anilide and bromide are
used in theoretical proportion, the hydrobromic acid in slight
excess. Sufficient alcohol is used to effect complete solution at
the boiling-point, and the hot solution cooled slowly. The
salt separates in long, colorless, doubly-terminated prisms.

Similarly to the cuprous chloride salt, it dissolves completely in alcohol, methyl alcohol and acetone, if a drop of hydrobromic acid is added. While drying, the crystals show temporarily on the surface that purple color so characteristic of copper compounds in presence of strong hydrobromic acid; but when dry they have at most a light grayish color. The dried salt is fully as stable as the corresponding chloride. On heating, it begins to darken at about 170°, and melts with decomposition from 185° to 195°, according to the rapidity of heating. Analysis gave the following results:

	Calculated.	I.	II.
			Found.
Cu	12.82	13.29	13.20
Br	32.36	32.39	32.41

$\left(C_6H_4\begin{smallmatrix}Br\\NHCOCH_3\end{smallmatrix}\right)_2$,HBrCuBr.—Parabromacetanilide gives with cuprous bromide a double salt of the above composition. The compound separates in long, colorless prisms, on cooling a hot solution of the constituents dissolved in a mixture of two volumes of alcohol and one volume of hydrobromic acid (sp. gr. 1.49). The substance thus prepared and dried *in vacuo* over sulphuric acid and potassium hydroxide, was used for a copper estimation, which gave 9.79 per cent. copper. For the above composition the theory requires 9.72 per cent. copper.

Formparatoluide and Cuprous Bromide.

$\left(C_6H_4\begin{smallmatrix}CH_3\\NHCHO\end{smallmatrix}\right)_2$,HBr+2CuBr.—This salt must be prepared in the cold and dried quickly. Three grams of formparatoluide dissolved in 12 cc. of formic acid (sp. gr. 1.20) were added to a solution of three grams of cuprous bromide dissolved in 24 cc. dilute hydrobromic acid (one volume HBr, sp. gr. 1.49, to one volume water). The salt separated at once in colorless, flat prisms. It was dried on a porous plate, then *in vacuo* over sulphuric acid and potassium hydroxide. It gave the following results on analysis:

	Calculated.	I.	II.
			Found.
Cu	19.88	19.57	19.68
Br	37.63	37.47	....

REVIEWS.

ORGANIC CHEMISTRY FOR THE LABORATORY. By W. A. NOYES, PH.D., Professor of Chemistry in Rose Polytechnic Institute, Terre Haute, Indiana. Easton, Pa.: Chemical Publishing Co. 1897. 257 pp. Price $1.50.

In his preface, the author in speaking of the object of this book, says: "Two distinct purposes have been kept in view. The first has been to furnish the beginner with sufficiently full and accurate directions, and clear, concise theoretical explanations of processes which have been found successful in practical laboratory experience. The second object has been to furnish the more advanced student and practical worker with a guide which will aid him in the selection of processes which are likely to be successful for the preparation of compounds which he may desire to use.

"It is for this second reason particularly that the number of preparations given is considerably greater than it would be profitable for the average student to prepare, and that the references to the literature have been made quite full."

The book has some points of similarity with those of Levy, of Gattermann, and of E. Fischer, but, of course, it differs from these in some respects. It does not deal with general principles in the same way that Gattermann's book does, and it covers more ground than is covered either by Levy, or by Fischer.

The matter dealt with is classified as follows: In Chapter I, Acids are presented; in Chapter II, Derivatives of Acids; in Chapter III, Halogen Compounds; in Chapter IV, Nitro Compounds; in Chapter V, Amines; in Chapter VI, Hydrazo, Azo, Diazo Compounds, etc.; in Chapter VII, Alcohols and Phenols; in Chapter VIII, Aldehydes, Ketones, and their Derivatives; in Chapter IX, Sulphonic Acids and Sulphine Compounds; in Chapter X, Hydrocarbons; in Chapter XI, Miscellaneous Compounds; and in Chapter XII, Qualitative Examination of Compounds and Reagents.

The book is clearly written, and the directions appear to be in every way satisfactory. There is sufficient discussion of the reactions to make them clear, and to direct the attention of the student to their relations to other similar reactions. If a student should conscientiously work through the course here laid down, he could not fail to become familiar with most of the important reactions of organic chemistry. It would, however, be difficult for him under ordinary circumstances to make all these preparations, and, as has been seen, the author does not expect this. The book can be cordially

recommended to teachers and to students, and those who are engaged in teaching and studying organic chemistry will do well to consult it frequently. It may well take its place by the side of those other laboratory guides that we are constantly using, namely, Gattermann, Levy, and Fischer.

There is one point which ought to be noted, and that is the evident carelessness in the proof-reading, as shown particularly in the misspelling of proper names. As examples of this the following incomplete list is given: Page 18, "Papow" instead of "Popoff," and "Hill" instead of "Hell;" p. 51, "Rugheimer" instead of "Rügheimer;" p. 83, "v. Meyer" instead of "V. Meyer"; p. 89, "Wislecenus" instead of "Wislicenus;" p. 101, "Lanteman" instead of "Lautemann;" p. 123, "Hoffmann" instead of "Hofmann," and this well-known name is also misspelled on pages 133, 138, 141 and 147; p. 160, "Fisher" instead of "Fischer;" p. 221, "Hantsch" instead of "Hantzsch." I. R.

CALCIUMCARBID UND ACETYLEN IN VERGANGENHEIT, GEGENWART UND ZUKUNFT. Von D. JOVAN P. PANAOTOVIC. Leipzig: Barth. 1897. 125 pp. Price 3.60 marks.

Any one interested in acetylene,—and who is not?—will find this book of much interest. The author is a believer in the gas, and tries to show that there are good reasons for his faith. The history of calcium carbide is sketched, and the relation between the scientific work of Moissan and the technical work of Willson is fully discussed. The main points of Willson's patent are stated and then the author indulges in this pleasant fling at Americans: "Willson scheint, wie seine Landsleute es oft thun, gar nicht nach seinem patentirten Verfahren zu arbeiten." However, in general, full justice is done to Willson's work, and it is clearly recognized that the rapid development of the carbide industry is due to this work. The question of the cost of the carbide and of the relative cost of acetylene gas and ordinary illuminating gas, is gone into quite fully, and anyone interested in this question will find much information of value in the book.

The various uses to which acetylene has been put and for which it has been recommended are then taken up. Under the head of the poisonous properties of acetylene the author reaches the conclusions that the gas is not as poisonous as it is generally supposed to be, and that accidents can be prevented by care and attention. The acetylene explosions that have done so much to prejudice the world against the gas are discussed in detail, the evidence being given and the conclusions of the courts in important cases. It appears that these explosions were due to want of experience in dealing with the

apparatus, and that they were not of such a character as to justify the wide-spread prejudice. The author says: '' In fact it is an easy matter to avoid the dangers by taking proper precautions.''

A very curious application of the carbide and of acetylene has been suggested, but it does not seem probable that this application will be of any service to the world. The suggestion is that life-preservers be supplied with calcium carbide, and so arranged that water can gain access to the rings in which the carbide is placed. On being thrown into water, of course, the acetylene would be generated and the vessels filled with gas.

<div align="right">I. R.</div>

MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. By the late DR. C. REMIGIUS FRESENIUS, Privy Aulic Counsellor and Professor, Director of the Chemical Laboratory at Wiesbaden. Authorized Translation by HORACE L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. New Edition, Thoroughly Revised. From the Sixteenth German Edition. John Wiley and Sons: New York. 1897.

The works of Fresenius on analytical chemistry need no introduction; for, either in the original or in the form of a more or less faithful translation, they are known to all chemists, and probably the majority of chemists have found them indispensable in their practice. For fifty years or more they have easily maintained a leading position as guides in analytical work. As such they have served the practical chemist, the teacher, and in many laboratories the student also. Their influence upon the education of more than one generation of chemists has undoubtedly been very great, but whether that influence has been good or bad is a question which may well be raised. Their phenomenal success can hardly be regarded as proof positive that their influence is wholly beneficent, for chemists and students of chemistry, like others, work along the lines of least resistance; and with them, as with others, the popular tools are those which save labor and hard thinking. In the works of Fresenius a complex subject has been successfully reduced to a finished but highly mechanical art. This is their great merit and the cause of their universal currency. But it may well be asked whether, by relieving the worker, as they do, from the necessity of an extensive study of the general subject, of treasuring his individual experiences, and of constantly exercising his constructive powers, they have not exerted a disastrous influence upon the laboratory study of chemistry as a mental discipline.

The translation is an admirable one.   H. N. M.

ELEMENTS OF CHEMISTRY. By RUFUS P. WILLIAMS, in charge of the
Chemical Department of the English High School, Boston, and
author of "Introduction to Chemical Science," "Chemical Experi-
ments, General and Analytical," and "Laboratory Manual of Inor-
ganic Chemistry." Boston and London: Ginn & Company. 1897.
412 pp. Price $1.20.

Here is another attempt to present the elements of chemistry
to the beginner as they should be presented. The book is
neatly gotten up, both as regards the type, paper, and illus-
trations. It has a fresh look about it, and will probably on
this account attract the attention of teachers. There are a
number of good features in the book, as there are in most
books on the subject that have appeared within the last few
years.

In addition to the descriptive part there are directions for a
large number of experiments to be carried out in the labora-
tory, in accordance with the usage which is becoming gen-
eral.

It is impossible to judge any book of this kind fairly with-
out testing it with students, and therefore it is not the pur-
pose of the writer of this notice to go into details on the sub-
ject of this particular book. The impression made upon the
writer, in general, is that the speculative part is a little be-
yond the beginner, and that the effect of using such a book
would be to give the student a wrong idea in regard to the
relation between facts and theory. It would be interesting to
hear the honest opinion of competent young students who
study for the first time Chapter X, for example, on valence,
in which he is given a definition of isomerism and views of
structure, as illustrated by benzene, the familiar hexagon
formula of which is exhibited. It is difficult enough for an
advanced student to form a clear conception of the meaning
of that and similar formulas, and in fact they are generally
misunderstood. What service the presentation of these ad-
vanced ideas to the beginner can be, it is extremely difficult,
not to say impossible, to see. Similarly, too much seems to be
made of writing equations, as presented in Chapter XI. Equa-
tions are, of course, well enough in their way, and are of ser-
vice to the chemist, but if their importance is magnified in the
lower stages of the course, the student is pretty sure to get the
idea that writing equations is chemistry. Other comments of
a similar kind might be made in regard to other parts of the
book, and the general statement may be made that it is
doubtful whether this book will be of much assistance in im-
proving the methods of teaching chemistry.   I. R.

THE DEVELOPMENT OF THE PERIODIC LAW. By F. P. VENABLE, PHD., F.C.S., Professor in the University of North Carolina. Easton, Pa.: Chemical Publishing Company. 1896. pp. 322. Price $2.50.

This book is the result of a conscientious effort on the part of the author to bring together the scattered literature on the subject of the Periodic Law, and as such it will be welcome to chemists everywhere. The importance of the Periodic Law is coming to be recognized more and more clearly year by year, and the law is coming to be used more and more as the basis of a scientific treatment of the facts of chemistry. It is therefore desirable that all chemists should have the opportunity to familiarize themselves with the development of our knowledge on the subject of the Law, and Professor Venable has done us a good service in pointing out the sources of information and giving us an idea of the contents of important articles that have a bearing upon this subject.

Probably all chemists will be surprised to learn how much has been written on the subject of regularities between the atomic weights or equivalent numbers. The author calls attention to the fact that "Before the atomic theory was formulated, numerical relations were proposed by Richter, the founder of Stoichiometry, between the equivalents obtained by him for the various bases and acids. This mathematical work of his served but little purpose beyond bringing the whole subject of his equivalents into some disrepute;" that after Prout, in 1815, pointed out the strange fact of the close approximation of the atomic weights to whole numbers, the so-called "Multiplenfieber" took possession of the chemical world. Then, through a series of years, Berzelius, Döbereiner, Turner, Penny, Meinicke, Dumas, Faraday, Kremers, Gladstone, Cooke, Kotikovsky, Lennsen, Newlands and many others, made suggestions bearing upon the regularities which were first clearly pointed out in a broad way by Lothar Meyer, and by Mendeléeff in 1869.

The history of the Periodic Law since that time is fairly familiar to most chemists, though it will again astonish many to find how many suggestions have been made during the past thirty years.

The reading of this book can be recommended to all chemists. It is interesting and instructive, and its study should be of assistance in causing the development of a more scientific habit than that which frequently characterizes chemists in their dealings with chemical facts.

The text is illustrated by a number of figures taken from original articles, and no pains have been spared to treat the subject in a clear and satisfactory manner.   I. R.

A Course of Practical Chemistry. By M. M. Pattison Muir, M.A. Fellow and Prælector of Chemistry in Gonville and Caius College, Cambridge. Part I.—Elementary. Longmans, Green & Co., London, New York and Bombay. 1897. 319 pp. Price 4s, 6d.

Mr. Muir has long been known as an earnest thinker and worker in the field of chemistry, and he has been trying, further, to improve the methods of teaching, his main effort being directed towards a more philosophical treatment of the subject than it commonly receives. There is no doubt that the presentation of the facts and principles of chemistry is generally scrappy and unsatisfactory, and many teachers are anxiously awaiting something better than they have at present in the way of a laboratory guide and text-book.

Mr. Muir, in his preface, says: "This book is offered to students and teachers as the first part of what I hope may prove to be a tolerably satisfactory and fairly systematic course of practical chemistry. It is the first portion of the result of very many attempts made during twenty-five years to devise a workable system of teaching in the laboratory."

This part is divided into three sections: Section I has to do with Experiments and Chemical Change ; Preparations of Various Compounds, Reactions of Acids, Alkalies, and Salts. Section II deals with Volumetric Estimations of Acids, Alkalies, Alkali Carbonates, Iron Salts, Chlorites, Calcium Compounds, and Iodine. Section III deals with Qualitative Analysis. The experiments described in the first four lessons need no special comment, as they are quite familiar and are utilized in many laboratory guides. In Lesson V, the matter of which is described thus, " Not-Mixtures divided into Compounds and Elements, Two Kinds of Chemical Changes— Building up and Breaking up," the experiments given are on the burning of magnesium in the air, the heating of lead in air, and the effect of heat on burnt mercury. These experiments are intended to show the student that the air takes part in the changes which are the subject of study ; and then in Lessons VII, VIII and IX a somewhat elaborate study of the Rusting of Iron is taken up. The underlying thought of these lessons is clear and logical, but it seems to the writer of this notice that the experiments are not well chosen. The rusting of iron is an extremely complex process, the nature of which we do not fully understand, but so far as it has been studied it is certain that it involves not only the action of the water and oxygen, but that of carbon dioxide upon the iron, and the kind of study that the beginner can give to the phenomenon is not such as to leave clear impressions upon his mind.

The same criticism can be made of several other experiments described in the book. While there is much to commend in the course laid down by Mr. Muir, it is questionable whether the course as a whole will give more satisfactory results than some of those which are now followed. Section I is the only one that calls for any comment, for in Section II we have to deal with familiar Volumetric Estimations, and in Section III Qualitative Analysis, and under neither of these heads is there likely to be much originality in the presentation.   I. R.

AN INTRODUCTORY COURSE IN QUANTITATIVE CHEMICAL ANALYSIS. By PERCY NORTON EVANS, PH.D., Associated Professor of Chemistry, Purdue University, LaFayette, Indiana. Boston and London : Ginn & Company, Publishers. 1897. 84 pp.

This little book is intended to assist teachers and students in dealing with the subject of Quantitative Analysis. After a brief introduction, in which the processes of weighing, filtering, and washing are briefly referred to, directions are given for the estimation of a number of elements and groups, as for example : Aluminium in alum, copper in copper sulphate, calcium in calcium carbonate, sulphuric acid in copper sulphate, chlorine in potassium chloride, phosphoric acid in sodium phosphate, potassium in potassium chloride, etc.

The course laid out is sufficiently full for the average student of chemistry, though hardly full enough for an advanced student who is looking forward to chemistry as his life work. The directions are clear and accurate, and the book ought to prove useful to those for whom it is intended.   I. R.

TAFELN UND TABELLEN ZUR DARSTELLUNG DER ERGEBNISSE SPEKTROSKOPISCHER UND SPEKTROPHOTOMETRISCHER BEOBACHTUNGEN. Herausgegeben von TH. W. ENGELMANN. Leipzig: Verlag von Wilhelm Engelmann. 1897.

This publication consists of two charts, with tables to accompany them, which are especially designed to render easy the recording of absorption-spectra and of photometric observations on them.

Plate I has along its upper edge a continuous prismatic spectrum with the principal solar lines, A, B, C, recorded on them. It also contains across the page other continuous spectra, forming colored backgrounds, on which the absorption-spectra of any substance can be at once recorded from the observations made by the spectroscope. In this way, on the same page, the absorption spectra of various substances may be recorded, or the changes in the spectra of any one substance may be noted.

Plate II contains along its upper edge a similar prismatic

spectrum, while the rest of the sheet is so arranged with lines vertical and horizontal, as to render it easy to make certain records of photometric observations or calculations corresponding to particular wave-lengths. In the tables which accompany these plates there are full directions as to their use and descriptions of various purposes for which they can be used. The Mathematical Tables are particularly designed to render easy any calculations and make it possible to record on the plate in suitable places those physical or chemical quantities which are most important and which are desired for further study. Among these quantities it may be well to mention :

First, the directly measured intensity of the transmitted light corresponding to different wave-lengths when the light has passed through various layers or various concentrations of coloring matter.

Second, the '' extinction coefficients,'' which may be calculated from these observations by means of the tables.

Third, the comparison between actual observed intensities and those calculated from other observations.

There are other uses to which these plates and tables may be put, and they will undoubtedly prove of great value to both chemists and physicists. To students in physical laboratories they furnish what has long been needed, a simple prismatic chart on which can be recorded not alone absorption-spectra, but also emission-spectra and the bands which are obtained by absorption through quartz and other substances where the rotation of the plane of polarization is to be studied.

<div align="right">J. S. A.</div>

THE PRINCIPLES OF MATHEMATICAL CHEMISTRY. THE ENERGETICS OF CHEMICAL PHENOMENA. By DR. GEORG HELM, Professor in the Royal Technical High School, Dresden. Authorized Translation from the German, by J. LIVINGSTON R. MORGAN, PH.D. (Leipzig), Instructor in the Brooklyn Polytechnic Institute. John Wiley & Sons: New York ; Chapman & Hall: London. 1897. pp. 228.

The rapid increase in the number of American and English students of physical chemistry has created a demand for an English version of this excellent work by Helm. When a student tries to read a book in a language with which he is not very familiar, upon a difficult subject, his energies are of necessity divided, and the result is not always entirely satisfactory. It may justly be claimed that the student should familiarize himself with the language, but, as this cannot be done in a day, we must meet the case as it is, rather than as it should be.

In order that a translation should be successful, it must, above all, be true to the original, and should, at the same

time, be expressed in clear, if not elegant, language.   That
the translation in hand always meets these demands satisfac-
torily cannot be maintained.

   On page 15, we read : '' Therefore thermochemical equa-
tions, strictly considered, should be given not only in a special
chemical state, but also in a special physical one,'' as the
translation of '' Daher muss in den thermochemischen Gleich-
ungen, streng genommen, nicht nur der chemische, sondern
auch   der   besondere   physikalische   Zustand angegeben
werden.''   On page 19, we find this statement : '' Although
heat is the form of energy which is produced in the greatest
amount by the chemical energy differences.''   The German
bears no direct relation to this : ''Wenn auch die Wärme die-
jenige Form der Energie ist in der die chemischen Energie-
unterschiede vorwiegend gemessen werden.''   We find on
page 41, '' They were, however, investigated in different
ways ;'' while the original says : '' Beide sind aber in sehr
verschiedenem Masse der Untersuchung unterworfen worden.''

   A statement is made on page 78, which is not only erro-
neous, but the English is almost unintelligible. ''If, however,
only one phase is present, then the other can only appear
when it has *not a smaller chemical intensity* than the other.''
The German is perfectly clear : '' Ist aber nur eine der
Phasen vorhanden, so kann der andere nur auftreten *wenn sie
kleinere chemische Intensität hat.''*

   If such discrepancies as these come out as the result of a
comparison of a few paragraphs of the English, with the
original, it is to be feared that the translation, in other places,
is not all that could be desired.

   While it is true that the translation of a technical mathe-
matical work, like the one under consideration, is not a sim-
ple task, yet it does seem that we could reasonably demand a
better product than has been furnished.   HARRY C. JONES.

CORRECTION.

   Vol. **19,** p. 891, line 17 from bottom : *For* ''lead ''*read* ''lead
oxide.''

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ON THE ACTION OF ACETIC ANHYDRIDE ON PHENYLPROPIOLIC ACID.

BY ARTHUR MICHAEL AND JOHN E. BUCHER.

Several years ago,[1] we showed that acetic anhydride reacts with acetylenedicarboxylic acid to form the anhydride of acetoxylmaleïc acid, and that this compound gives oxalacetic acid on treatment with water. If acetic anhydride should react with phenylpropiolic acid in an analogous manner, the anhydride of β-acetoxylcinnamic acid would be formed, and this compound on decomposing with water would yield a β-hydroxycinnamic acid. It seemed of theoretical interest to ascertain whether a product obtained in such a manner is identical with the benzoylacetic acid[2] gotten by saponification of its ester, but this object was not realized, as it was apparent from the preliminary experiments that acetic anhydride reacts on phenylpropiolic acid, in an entirely different manner than on acetylenedicarboxylic acid.

The new product has the composition of phenylpropiolic anhydride, but its properties showed that such a constitution is impossible. On treating it with alkalies it goes into solution, and addition of a mineral acid gives a precipitate of the original anhydride, not of phenylpropiolic acid, which

[1] Ber. d. chem. Ges., **28**, 2511.   [2] Perkin: J. Chem. Soc., **45**, 174.

should be formed if it were the anhydride of this acid. This behavior shows also that at least two molecules of phenyl-propiolic acid enter into the reaction, and also that the substance cannot be the anhydride of symmetrical triphenylmesic acid. The reduction of the substance in alkaline solution yields an acid that no longer spontaneously gives an anhydride, and with the composition of the truxillic acids; but not identical with any known acid of that series. By an investigation of the original anhydride we have been able to classify it as a derivative of naphthalene, and we reserve the discussion of this peculiar reaction until we describe our experimental results.

Preparation of the Anhydride, $C_{18}H_{10}O_3$.

The phenylpropiolic acid used in our work was usually made by the action of alcoholic potash on $\alpha\beta$-dibromhydrocinnamic ester, as we found that the impure acid obtained in this way gave the new product in a pure condition. In our earlier experiments the acid and anhydride were heated in sealed tubes to 100°, but later we found that the reaction takes place easily on boiling these substances in a flask connected with a return cooler. The method of procedure can be best illustrated by describing two of the actual experiments in detail.

28.5 grams of phenylpropiolic acid and 57.9 grams of acetic anhydride were heated in a sealed tube at 100° for seven hours. The acid went into solution at once, and after warming for some time a substance began to separate in large, transparent, tabular crystals. The cold tube showed no pressure on opening, and the crystals, after washing with a little acetic acid and drying, weighed 13.6 grams. The mother-liquor was distilled off *in vacuo* at 100°, and the oil thus obtained became solid on standing in the cold. On treating with a small quantity of cold absolute ether all the substance, except 0.39 gram, went into solution, and the insoluble substance proved to be the same product as the 13.6 grams. The ether was driven off from the filtrate *in vacuo*. On standing the thick oil solidified, and was purified by washing with dry benzene, then crystallizing from a hot carbon tetrachloride and benzene. It forms crystals hav-

ing a cubical appearance, and melting at $72°–74°$. An analysis of the substance, dried *in vacuo*, gave the following figures:

0.18379 gram substance gave 0.3325 gram CO_2, and 0.0480 gram H_2O.

	Theory for $(C_6H_5—CH—CBr—CO)_2O$.	Found.
C	49.52	49.36
H	2.93	2.90

The results show that the compound has the composition of the anhydride of bromcinnamic acid, and to ascertain to which of the acids it corresponds, it was dissolved in cold alkali, and the precipitate formed by addition of hydrochloric acid crystallized from hot water. The acid so obtained melted at $120°$, and possessed the other properties of allo-α-bromcinnamic acid. Its identity was further confirmed by an analysis.

	Theory for $C_6H_5—CH—CBr—COOH$.	Found.
C	47.58	47.88
H	3.07	2.98

The formation of this anhydride is evidently due to the presence of allo-α-bromcinnamic acid in the phenylpropiolic acid. In decomposing $\alpha\beta$-dibromhydrocinnamic ester with caustic potash a mixture of α- and allo-α-bromcinnamic acids are formed, and of these two acids only the higher-melting isomer is readily further split into phenylpropiolic and hydrobromic acids. For this reason the method described by Perkin[1] for the preparation of phenylpropiolic acid always gives a mixture of this acid and allo-α-bromcinnamic acid; in fact, some of our preparations contained as much as 30–40 per cent. of the brom-acid. This mixture, however, may be satisfactorily used in the reaction, as it is easy to separate the two products, and the allo-α-bromcinnamic anhydride may be converted by esterization with hydrochloric acid into α-bromcinnamic ester, from which product phenylpropiolic acid may be obtained in almost theoretical amount. To prepare the substance in an open flask, connected with a return-condenser, 100 grams each of impure phenylpropiolic acid and acetic anhydride were heated until the liquid began to boil, when the burner was

[1] J. Chem. Soc., **45**, 142.

removed. The reaction once begun evolved considerable heat, so that the solution kept boiling about five minutes; on cooling, crystals began to separate, when the boiling re-commenced, and then continued for some minutes longer. On standing, 45 grams of pure substance were deposited, and by boiling the mother-liquor for several hours, a further deposit of 6 grams was obtained. In our subsequent preparations we boiled the solution for one-half hour after the heat of the reaction had moderated, and found this heating sufficient to complete the decomposition. The yield was about 50–60 per cent. of the phenylpropiolic acid taken, but if a pure acid were used it would probably not be far from the theoretical. After washing the crystals with acetic acid, they were powdered, and crystallized from boiling cumene.

I. 0.1657 gram of substance, dried *in vacuo* at 100°, gave 0.4793 gram of CO_2 and 0.0547 gram of H_2O.

II. 0.1503 gram of substance, dried *in vacuo* at 100°, gave 0.4362 gram of CO_2 and 0.0490 gram of H_2O.

	Theory for $C_{18}H_{10}O_2$.	Found. I.	II.
C	78.83	78.89	79.15
H	3.65	3.67	3.62

The crystals obtained in the preparation of the substance are transparent, hard, rectangular prisms, many of them with truncated angles, and melting at 255°, although it begins to soften at 230°. In this state the substance is very resistant to the action of ordinary solvents, even to alkaline solutions, but may be recrystallized from boiling acetic anhydride or cumene. If the substance is brought into solution by boiling with alkalies, and the solution acidified, it comes down as a pasty mass, which soon solidifies, and in this condition it is easily soluble in alcohol, glacial acetic acid, acetic ester, acetone and sodium carbonate. The difference in solubility is due, however, to a different state of aggregation, and not to a chemical change. Heated in an open tube, it boils and condenses on the sides of the tube, without essential decomposition.

The molecular weight was determined according to Eyk-man's method, and the following results obtained:

	Phenol. Grams.	Substance. Grams.	Δ.	Molecular weight.
I	12.9062	0.1770	0°.39	267
II	12.8100	0.2694	0°.62	258
III	12.7972	0.3534	0°.81	259

Mean = 261

Calculated for $C_{18}H_{10}O_3$ = 274

Salts of the Acid, $C_{18}H_{12}O_4$.

It has been already noticed that the substance can be dissolved in alkalies, when it goes over into a salt of an acid, and on addition of a mineral acid to this solution the original anhydride is precipitated. This relationship is similar to that shown by certain unsaturated, dibasic acids like the dialkylmaleïc acids; and the above property seemed to indicate that the unstable carboxyls are in a side chain, as the property of forming an anhydride spontaneously has not been observed with carboxyls existing in the benzene nucleus.

The sodium salt was prepared by boiling the anhydride in a flask with a return-condenser, with the theoretical amount of pure sodium hydrate, dissolved in ten parts of water, until complete solution, and filtering the thick mass of crystals under pressure, which were deposited as the solution cooled. These crystals were washed once with a little water, then thoroughly with 50 per cent. alcohol. A further quantity may be obtained by adding an excess of caustic soda to the filtrate, as it is much less soluble in an excess of alkali than in water. The salt forms white, glittering, prismatic plates, that are obliquely truncated, and in aqueous solution it does not show the permanganate test for unsaturated acids.

I. 0.6262 gram air-dried salt, dried first at 100°, then 130°, and finally at 165°–170°, under 20 mm., lost 0.1197 gram H_2O.

II. 0.5872 gram air-dried salt gave 0.1994 gram Na_2SO_4.

III. 2.3640 grams air-dried salt gave 0.8108 gram Na_2SO_4.

	Theory for $C_{18}H_{10}O_4Na_2.4\frac{1}{2}H_2O$.	I.	Found. II.	III.
H_2O	19.65	19.11	....	....
Na	11.04	....	11.12	11.12

The barium salt was made by adding barium chloride to a solution of the sodium salt, and was deposited as a granular pre-

cipitate, which seen under the microscope consisted of obliquely-truncated prisms.

I. 0.4544 gram of air-dried salt, heated gradually to 165°, lost 0.0558 gram H_2O.

II. 0.4290 gram of air-dried salt gave 0.2002 gram $BaSO_4$.

| | Theory for | | Found. | |
	$C_{18}H_{10}O_4Ba.3H_2O$.	$C_{18}H_{10}O_4Ba.4H_2O$.	I.	II.
H_2O	11.23	14.43	12.27	....
Ba	28.50	27.46	....	27.44

The water of crystallization is evidently expelled with difficulty, which accounts for the low results in the direct determination.

In a similar manner the calcium salt was obtained as a crystalline precipitate.

0.7175 gram salt, air-dried, lost 0.0846 gram H_2O at 200°.

0.7175 gram salt, air-dried, gave 0.2551 gram $CaSO_4$.

| | Theory for | Found. | |
	$C_{18}H_{10}O_4Ca.3H_2O$.	I.	II.
H_2O	14.06	11.79	....
Ca	10.42	....	10.45

The salt evidently contains three molecules of water of crystallization, all of which is not expelled at 200°.

Solutions of silver nitrate and the sodium salt give a white, granular precipitate of the silver derivative, which changes but slowly on exposure to light.

0.2319 gram of air-dried salt gave 0.0956 gram Ag.

0.2846 gram of air-dried salt lost 0.0018 gram H_2O when heated to 100° for 45 minutes, and 0.1203 gram Ag.

| | Theory for | Found. | |
	$C_{18}H_{10}O_4Ag_2$.	I.	II.
Ag	42.59	41.22	42.59

All of the above salts give the original anhydride on decomposition with acids, and it is evident from these results that the dibasic acid, $C_{18}H_{12}O_4$, cannot exist in a free state, but decomposes on liberation from its salts into the anhydride, $C_{18}H_{10}O_3$, and water.

To obtain the methyl ester the anhydride with four parts by weight of methyl alcohol and one-half part of sulphuric acid was boiled for four hours. On standing in a cool place

crystals were deposited, which, after treatment with sodium carbonate solution, consisted of the ester. The mother-liquor, poured into water gave a pasty mass, which gradually solidified on being rubbed with a pestle, under a solution of sodium carbonate. The yield of ester obtained in this way is far from satisfactory, being only about one-third the weight of the anhydride used in the experiment. A better result was gotten by treating the air-dried silver salt in a sealed tube with methyl iodide. The reaction proceeded in the cold, and was complete after heating one hour at 100°. The precipitate, consisting of silver iodide and methyl ester, was extracted with hot alcohol, and the crystals deposited on cooling treated with a cold solution of sodium carbonate. The insoluble residue was purified by several crystallizations from alcohol, and gave the following analytical results :

0.2549 gram ester gave 0.6964 gram CO_2 and 0.1153 gram H_2O.

0.2395 gram ester gave 0.6572 gram CO_2 and 0.1092 gram H_2O.

	Calculated for $C_{16}H_{10}(COOCH_3)_2$.	Found.	
		I.	II.
C	75.00	74.63	74.84
H	5.00	5.05	5.07

The ester crystallizes from alcohol in white prisms, that melt at 118°–120°. It dissolves readily in hot methyl alcohol and ethyl alcohol, and carbon tetrachloride, less readily in hot ether ; in these solvents, when cold, it is moderately soluble. Saponified with alkalies the solution gave a precipitate of anhydride on acidifying. A solution of ester in carbon tetrachloride was slowly acted on by bromine on exposure to light, but an addition-product was not formed.

Molecular weight determinations[1] of the ester, according to Eykman's method, gave the following results :

[1] We are indebted to Dr. V. L. Leighton for these determinations, as well as for those of the anhydride.

	Phenol. Grams.	Substance. Gram.	Δ.	Molecular weight.
I	11.8128	0.1422	$0°.2575$	355
II	11.7200	0.6652	$1°.3625$	317
III	11.6900	0.8440	$1°.6975$	323

Mean = 332
Theory = 320

Primary Product of the Action of Acetic Anhydride on Phenyl-propiolic Acid.—In one of our experiments we heated pure phenylpropiolic acid with four times its weight of acetic anhydride in a sealed tube for a short time at 100°. The acid went into solution, but no anhydride was deposited on cooling. The product was distilled *in vacuo*, and remained liquid until almost all the acetic anhydride was expelled, when, as the water-bath was heated to almost 100°, the residue solidified, and now consisted of the anhydride and a small amount of oil. Evidently the anhydride must have been formed during the process of heating on the water-bath, as otherwise it would have been deposited as the contents of the tube were cooled. We were led by this result to endeavor to isolate the product first formed in this reaction.

A quantity of pure phenylpropiolic acid was placed in a sealed tube with five times its weight of acetic anhydride, and, after standing five days at ordinary temperature, the product was evaporated, *in vacuo*, over caustic soda, when the greater part of the phenylpropiolic acid was recovered unchanged.

A second quantity of phenylpropiolic acid was dissolved in four parts of acetic anhydride, allowed to stand for twelve hours, then evaporated at ordinary temperature *in vacuo*, and this operation repeated twice. After the last treatment it was allowed to stand in a partial vacuum for a week, and then consisted of an oil and a small quantity of a solid, which was found to be a mixture of the anhydride and phenylpropiolic acid. On further standing more of these substances slowly separated from the oil, and, as it was apparently decomposing with the formation of the anhydride, the oil was decanted and analyzed.

0.1587 gram oil gave 0.4087 gram CO_2, and 0.0654 gram H_2O.

	Theory for $C_{11}H_8O_3$.	Found.
C	70.27	70.24
H	4.27	4.59

The oil dissolved very slowly in a solution of sodium carbonate, quickly in caustic alkalies, and acids precipitated phenylpropiolic acid from these solutions. In the filtrates the presence of acetic acid was proven. The substance $C_{11}H_8O_3$ is evidently the mixed anhydride of acetic and phenylpropiolic acids, with the constitution C_6H_5—C—·C—CO—O—OC—CH_3.

Action of Aniline on the Anhydride, $C_{18}H_{10}O_3$.

The anhydride and aniline, in proportion of one to four equivalents, and some water were heated to 100°. The anhydride went into solution, and after a time a solid substance was deposited, which was purified by crystallization from alcohol.

0.1375 gram substance gave 0.3947 gram CO_2, and 0.0612 gram H_2O.

	Theory for $C_{18}H_{10}O_3.NH_2C_6H_5$.	Found.
C	78.47	78.79
H	4.63	4.95

The substance forms transparent crystals, that melt at 194° with decomposition. It is insoluble in water, and moderately in cold alcohol. Aqueous caustic soda does not effect solution, but converts it into a sticky mass. This property of the substance is not in accordance with the view that it is the acid anilide of the acid $C_{18}H_{10}(COOH)_2$. The substance was not further examined.

Action of Sodium Amalgam on the Sodium Salt, $C_{16}H_{10}(COONa)_2$.

A simple conception of the formation of the anhydride,

$C_{16}H_{10}$ $\begin{array}{c} CO \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ CO \end{array}$ O from phenylpropiolic acid is the polymeriza-

tion of two molecules to form a four-ring derivative. Such a tetramethine derivative should pass over on reduction to a tetramethylene product, which might be identical with one of the truxillic acids of Liebermann.[1] Contrary to this constitution is the comparative stability of the sodium salt towards potassium permanganate, but this indifference might possibly be due to the ring-constitution of the substance, as the permanganate test is characteristic only for fatty $\alpha\beta$-unsaturated acids. Twenty grams of the anhydride were dissolved in 8 grams of sodium hydrate, the solution diluted to 800 cc., and 800 grams of a four per cent. sodium amalgam gradually added. It is necessary to use a large excess of sodium amalgam, as otherwise the reduction-product will contain a considerable proportion of unreduced acid. The sodium salt of the reduced product is rather insoluble in strong alkali, so that the salt separated as prismatic crystals near the amalgam, but it gradually rose, and dissolved in the less concentrated layer of the liquid. The solution was partially neutralized, filtered, and acidified with sulphuric acid, when an oily substance was deposited, which gradually turned solid. This product is soluble in acetone, and is precipitated on concentrating the solution, or by adding benzene to it, but this method of treatment is not satisfactory, owing to the tendency of the substance to form a syrup. It is preferable to treat with hot acetic acid in sufficient quantity to dissolve almost the entire product, pour off from the undissolved substance, and recrystallize the precipitate formed on cooling, from the same solvent, until its melting-point becomes constant. The mother-liquors gave some more of the product, but the last part was always more or less gummy. It was analyzed with the following result :

I. 0.1660 gram substance, dried at 100°, gave 0.4440 gram CO_2, and 0.0806 gram H_2O.

II. 0.1936 gram substance, dried at 100°, gave 0.5149 gram CO_2, and 0.0986 gram H_2O.

	Theory for $C_{18}H_{16}O_4$.	Found. I.	II.
C	72.97	72.93	72.54
H	5.40	5.39	5.55

[1] Ber. d. chem. Ges., **21**, 2342 ; **22**, 124 and 2240.

The new acid forms white crystals that melt, under decomposition, at 200°–202°, but the melting-point depends on the rapidity of heating, and it melts with slow heating at 195°–198°. It is easily soluble in acetone and acetic ether, difficultly in cold water, and insoluble in carbon tetrachloride and benzene.

Neutralized with aqueous ammonia, its solution gave white crystalline precipitates with solutions of barium, calcium, and mercuric chlorides. Silver nitrate precipitates a white salt, that becomes crystalline on warming. It was dried *in vacuo,* then for thirty minutes *in vacuo* at 100°, and analyzed.

0.6824 gram salt gave 0.2933 gram Ag.

	Theory for $C_{18}H_{14}O_4Ag_2$.	Found.
Ag	42.83	42.35

A further reduction by sodium amalgam does not take place ; as we boiled a solution of the sodium salt with a large excess of amalgam, and recovered only the unchanged acid, $C_{18}H_{16}O_4$. We also found that the acid, when heated with concentrated hydriodic acid and amorphous phosphorus, undergoes no change.

Anhydride of the Acid, $C_{18}H_{16}O_4$.

Three grams of acid and six grams of acetic anhydride were heated to 170° in a sealed tube. On cooling, the tube opened without pressure, and contained a clear solution that partially solidified on rubbing with a glass rod. The crystals were washed with acetic anhydride, and then recrystallized from this solvent. For analysis it was dried *in vacuo* at 100°.

0.1529 gram substance gave 0.4340 gram CO_2, and 0.0736 gram H_2O.

	Theory for $C_{18}H_{14}O_3$.	Found.
C	77.15	77.41
H	5.06	5.33

The anhydride is a white crystalline solid, that melts at 145°–150°. It dissolves on warming with caustic soda, and mineral acids precipitate the original acid from this solution. The acid $C_{18}H_{16}O_4$ is not only iso-

meric with the truxillic acids, but resembles the β-acid of this group in its properties. It is not identical with it, however, as β-truxillic anhydride[1] has different properties from the compound just described, a conclusion which is confirmed by the behavior of our acid towards aniline. Equal weights of acid and base were boiled for fifteen minutes. On cooling, a sticky mass was obtained, which was treated with dilute hydrochloric acid and caustic soda, and then washed with dilute alcohol. The substance remained in a semi-solid condition, and could not be brought to crystallize, whereas the β-truxillanil forms a crystalline, high-melting compound.[2]

Behavior of the Acid, $C_{18}H_{16}O_4$, *on Oxidation with Potassium Permanganate.*

Two grams of the acid were dissolved in an excess of dilute caustic soda and 120 cc. of a 5 per cent. solution of permanganate, added in six portions, the solution being allowed to become colorless before each new addition. The first 60 cc. of the permanganate were reduced almost entirely, while the last 20 cc. were only nearly decolorized after twenty-four hours; a further addition of 5 cc. made the solution retain the permanganate color, even after standing two days. After each decolorization the manganese dioxide was filtered, washed with water, and examined for organic matter, but only the first precipitate contained a trace, which was insoluble in sodium carbonate, and did not give the alcoholic potash test for benzil. On evaporating the filtrates and acidifying, a yellowish, viscous product separated, which could not be brought into a crystalline state, nor purified, and was therefore not further examined. This experiment further established the fact that our product is not identical with β-truxillic acid, as that substance gives benzil when treated as above.[3]

Reduction of the Anhydride, $C_{18}H_{10}O_3$, *in Acetic Acid Solution.*

Five grams of anhydride were dissolved in 50 cc. of acetic

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[1] Liebermann and Sachse : Ber. d. chem. Ges., **26**, 835.

[2] Liebermann and Sachse, *loc. cit.*, used anhydride in their experiment, but there can be but little doubt that the acid would give the same result. We obtained a neutral substance, like an anil, which certainly showed entirely different chemical and physical properties from their product.

[3] Liebermann : Ber. d. chem. Ges., **22**, 2254.

acid and 20 grams water, and 15 grams zinc dust added. After boiling for four hours in a flask with return-cooler, 10 cc. water were added, and the mixture again heated for three hours. On pouring into dilute sulphuric acid, an organic substance was deposited, which melted from 130°–190°. The crude product was rubbed for several minutes with a 5 per cent. solution of sodium carbonate, filtered, and the residue again treated in the same way, when all the acid was removed. The insoluble residue was purified by several crystallizations from alcohol and analyzed.

0.1519 gram substance, dried at 100°, gave 0.4614 gram CO_2, and 0.1519 gram H_2O.

	Theory for $C_{18}H_{12}O_2$.	Found.
C	83.08	82.84
H	4.62	4.63

The white crystalline substance melted at 135°–137° without decomposition. Its behavior towards sodium carbonate shows that it is a neutral body, and it follows from this property and its composition, that it must be a lactone, formed by replacing an oxygen of carbonyl by two hydrogen atoms.

Oxidation of the Anhydride, $C_{18}H_{10}O_3$, *with Potassium Permanganate.*

A large number of oxidation experiments, in which the conditions were variously modified, were made in the hope that the results would throw some light on the constitution of the anhydride. The sodium salt of the acid, $C_{18}H_{14}O_4$, is considerably more easily oxidized by permanganate than that of the acid, $C_{18}H_{12}O_4$; in fact the first product behaves towards this reagent like an unsaturated fatty acid, whereas the second could not be so classified. To judge from this property, the unsaturated part of the acid, $C_{18}H_{12}O_4$, cannot belong to an unsaturated fatty side chain, and the relation of the reduced to the original body, in its susceptibility to oxidation, agrees with the assumption that the reduction has gone on in the aromatic nucleus of the compound.

Ten grams of the anhydride, $C_{18}H_{10}O_3$, were dissolved

in an excess of caustic soda, the solution diluted and made neutral by addition of sulphuric acid. To this solution a 5 per cent. solution of potassium permanganate, in portions of 10 cc., were added, waiting for decolorization before adding a fresh portion. The first portions of the oxidizing agent were reduced in ten to twenty minutes, but towards the end the oxidation proceeded very slowly. In all, 54 grams of potassium permanganate were used until no, or only extremely slow, oxidation occurred. The solution was decolorized by addition of sodium sulphite, filtered, concentrated on the water-bath, acidified with sulphuric acid, and extracted with ether. On removing the ether, a very viscous oil remained, which, placed in a vacuum, formed a large bubble, expanding until the upper part of the bell-jar was almost completely filled. On long standing in a vacuum the product became friable, and could be pulverized, and then weighed 14 grams. This product was dissolved in dry acetone, and the precipitate, formed by slow evaporation, dried and analyzed (I).

In a second experiment 17 grams of anhydride were dissolved in caustic soda, the solution diluted to 1500 cc., and 90 grams of powdered potassium permanganate added. The solution was warmed on a water-bath, shaken until all the permanganate had gone into solution, and then heated four hours to boiling in a flask with a return-cooler. On cooling, the solution was decolorized with sodium sulphite, and worked up as described in the preceding experiment. 22 grams of crude product were obtained. This was dissolved in dry acetone and some benzene added, when part of the substance came down in crystalline form. The mother-liquor gave a syrup which, as it could not be brought to crystallize, was dissolved in alkali, acidified and extracted with ether. A friable product was obtained, which was boiled with glacial acetic acid, to remove a sticky substance, dissolved in dry acetic ester and some glacial acetic acid added to the solution. On warming gently the acetic ester was gradually expelled, and a crystalline substance separated. It was filtered, washed with a mixture of acetic ester and acid, and, after drying *in vacuo* at 100°, it was analyzed (II).

As the above product did not show a sharp melting-point, it began to turn yellow at 230°, and was not completely melted until 280°; the rest of it was dissolved in hot acetic ester and recrystallized after addition of acetic acid. There was no change in the melting-point, and an analysis (III) showed that the substance was in a pure state.

I. 0.1263 gram substance gave 0.2687 gram CO_2, and 0.0395 gram H_2O.

II. 0.1608 gram substance gave 0.3424 gram CO_2, and 0.0500 gram H_2O.

III. 0.1626 gram substance gave 0.3455 gram CO_2, and 0.0495 gram H_2O.

	Theory for $C_{18}H_{10}O_8$.	Theory for $C_{18}H_{12}O_9$.	I.	Found. II.	III.
C	58.18	58.01	58.02	58.07	57.95
H	3.33	3.23	3.47	3.45	3.38

The white, crystalline acid is slowly soluble in cold, quickly in hot, water. Obtained by evaporation of its solution in ether, it is difficult to get it back into solution by the same solvent, but it dissolves readily in acetic ester and alcohol, and is almost insoluble in benzene, acetic acid, acetone, chloroform and carbon tetrachloride. After crystallization from a mixture of acetic ester and acid, it only dissolves in acetic ester and acetone after protracted boiling. The acid may be heated to 150°–160° with concentrated hydriodic acid and phosphorus without undergoing change.

Silver Salt.—This derivative was made by adding aqueous silver nitrate to a neutral solution of the acid in ammonia, and forms a white precipitate.

I. 0.6467 gram salt, dried to constant weight *in vacuo*, gave 0.3637 gram Ag.

II. 0.5023 gram vacuum-dried salt did not lose weight by drying for one-half hour at 100°, and gave 0.2823 gram Ag.

III. 0.5750 gram salt, dried for a short time *in vacuo*, gave 0.3262 gram Ag.

	Theory for $C_{12}H_6(COOAg)_4$.	Theory for $C_{14}H_8(COOAg)_4$.	I.	Found. II.	III.
Ag	56.99	55.10	56.24	56.20	56.73

Barium Salt.—Obtained from the ammonium salt as a white crystalline precipitate by addition of barium chloride. This

salt often requires considerable time before separating, but heating the solution brings it down at once. The following experiments afford an approximate determination of its solubility; 0.2 gram neutralized acid in 160 cc. water (1 acid to 800 water) gave no precipitate in the cold, but one was formed on heating, that did not redissolve on standing in the cold. In another test, with double the quantity of water, no salt was formed, even after heating the solution.

I. 0.4577 gram air-dried salt, lost 15.6 per cent. water at 190°,[1] and gave 0.2885 gram $BaSO_4$.

II. 0.4000 gram air-dried salt lost 15.45 per cent. water at 200°, and gave 0.2525 gram $BaSO_4$.

III. 0.2512 gram air-dried salt gave 0.1591 $BaSO_4$.

	Theory for $C_{16}H_6O_8Ba_2.8H_2O$	I.	Found. II.	III.
Ba	36.86	37.07	37.24	37.12

The *calcium salt* is soluble in water; and a *lead salt* is deposited as an insoluble, white substance by addition of lead acetate to a solution of the acid.

The results obtained with the silver salt indicate that the acid is tetrabasic, and this view as was confirmed by titration of the acid with caustic potash. 0.1017 gram crystallized oxalic acid required 5.96 cc. of the alkaline solution in use.

0.1019 gram of the acid required 4.45 cc. potassium hydrate solution. Calculating from these results the molecular weight of the tetrabasic acid would be 337.5, while the molecular weight of $C_{16}H_{10}O_8$ is 330. As the molecular weight of the acid deduced from the analyses of the silver salts is 333.5, it is very probable that the acid is tetrabasic, providing its molecular weight is not a multiple of the above number.

Methyl Ester.—We prepared this compound in the hope of obtaining a derivative of the acid with a sharp melting-point, and to establish its molecular weight with greater certainty. The vacuum-dried silver salt, and an excess of methyl iodide, and some dry ether, were sealed in a tube, and warmed gently at first, finally heated to 100° for an hour. On standing over night, large crystals had separated from the supernatant liquid. Absolute alcohol was added to the mixture and, after heating

[1] The water of crystallization cannot be completely expelled without decomposition of the acid.

for some time, it was filtered hot. On cooling considerable substance separated, but a minute quantity of silver iodide was also deposited, which could not be perfectly separated from the ester by repeated crystallizations from alcohol. The greater part of the alcohol was driven off, the precipitate dissolved in boiling chloroform, and the solution filtered from the insoluble silver iodide. The product was obtained pure by recrystallizing three times from carbon tetrachloride.

I. 0.1503 gram ester, dried at 100°, gave 0.3421 gram CO_2, and 0.0650 gram H_2O.

II. 0.1946 gram ester, dried at 100°, gave 0.4398 gram CO_2, and 0.0838 gram H_2O.

III. 0.2160 gram ester, dried at 100°, gave 0.4902 gram CO_2, and 0.0912 gram H_2O.

IV. 0.2025 gram ester, dried at 100°, gave 0.4606 gram CO_2, and 0.0940 gram H_2O.

	Theory for $C_{12}H_6(COOCH_3)_4$.	Theory for $C_{14}H_8O(COOCH_3)_4$.	I.	II.	III.	IV.
C	62.18	61.68	61.91	61.66	61.91	62.03
H	4.66	4.67	4.69	4.79	4.69	5.19

The ester crystallizes in large, transparent rhombohedrons, that melt at 130°–133°. It is soluble in hot alcohol, methyl alcohol, chloroform and carbon tetrachloride; only moderately in these solvents when cold. The molecular weight of the ester was determined by the freezing-point method, glacial acetic acid being used as the solvent.

	Acetic acid. grams.	Substance. gram.	Δ	Molecular weight.
I	20	0.5056	0°.28	351
II	20	0.0740	0°.47	400

Mean $= 376$
Theory for $C_{12}H_6(COOCH_3)_4 = 386$
Theory for $C_{14}H_8O(COOCH_3)_4 = 428$

The difference between the carbon percentages in the above formulae is only 0.5 and that of hydrogen is practically the same, and although the analytical results indicate that the acid contains sixteen atoms of carbon, it is impossible to decide with certainty between the two possible formulae. The evidence from the molecular weight determinations is also in

favor of the simpler composition, but here too the figures are too close for a sure proof. These last results prove, however, that the acid is tetrabasic, as was made probable from the study of its metal salts.

Benzyl Ester.—A little less than the theoretical amount of benzyl iodide, dissolved in dry ether, was added gradually to the dry silver salt, and the tube containing it kept cool during the operation. It was then sealed, and heated for 12 hours at 100°. The silver iodide was filtered, and the oily filtrate shaken with dilute, aqueous sodium carbonate. On standing three layers were formed, the middle one consisting of the alkaline solution. The upper layer was warmed until the ether was driven off, and a crystalline substance left, which was crystallized from glacial acetic acid.

0.1586 gram ester gave 0.4445 gram CO_2, and 0.075 gram H_2O.

	Theory for $C_{12}H_6(COOCH_2C_6H_5)_4$.	Theory for $C_{14}H_8O(COOCH_2C_6H_5)_4$.	Found.
C	76.52	70.59	76.26
H	4.93	4.31	5.25

The ester forms a white crystalline substance, that melts at 114–118°. Heated with alkalies, in a sealed tube at 100°, the ester is saponified, and the original acid was regained from the product of the reaction.

The large difference between the carbon-percentages in the above formulae, almost 6 per cent., and the analytical results obtained in the combustion of the ester, leave no doubt that the orginal acid has the composition, $C_{12}H_6(COOH)_4$.

Anhydride of the Acid, $C_{12}H_6(COOH)_4$.

A portion of the acid was heated with twice its weight of acetic anhydride to 150°–170° for three hours, and the product of reaction evaporated to dryness *in vacuo*. The residue was washed with a little benzene, and then crystallized from boiling xylene.

0.1373 gram substance, dried at 100°, gave 0.3263 gram CO_2, and 0.0310 gram H_2O.

	Theory for $C_{12}H_6[(CO)_2O]_2$.	Found.
C	65.31	64.91
H	2.04	2.51

The anhydride is a light-yellow crystalline body. Treated with alkalies it goes into solution, forming a salt of $C_{12}H_6(COOH)_4$.

Hydrocarbon from the Acid, $C_{12}H_6(COOH)_4$.

An intimate mixture of barium salt of the acid with about twice its weight of dry barium hydrate was rapidly heated in a glass tube, a current of hydrogen being passed over it at the same time. The distillate was extracted with dilute sodium hydrate, then with ether, and the solid residue remaining after evaporation of the solvent, crystallized several times from alcohol. The hydrocarbon possessed the melting-point (71°) and the other properties of diphenyl, and its identity with that substance was further confirmed by analysis.

0.0757 gram substance gave 0.2590 gram CO_2, and 0.0467 gram H_2O.

	Theory for $C_{12}H_{10}$.	Found.
C	93.50	93.31
H	6.49	6.85

It is evident from the conversion of the acid $C_{12}H_6(COOH)_4$ into diphenyl that the acid is a tetracarboxyl derivative of this hydrocarbon, but it still remains to show the distribution of the carboxyl in the molecule. Further investigation of the acid was rendered unnecessary, as its full constitution conclusively follows from the constitution proven farther on for the original anhydride.

Second Acid Formed in the Oxidation of the Anhydride, $C_{14}H_{10}(CO)_2O$.

In all our oxidation experiments we invariably obtained a sticky mass in the acetic acid mother-liquors, which on standing in a vacuum gradually became friable, but could not be brought into a crystalline condition. The solubilities of this product left no doubt as to its difference from the oxidation-product already described, although there was no certainty of a perfect separation of the two products by the method used. The examinations of the salts of the two products showed that the separation could easily be effected by means of the barium salts, as this derivative of the amor-

phous acid is very soluble in water, while the crystalline acid, as is already shown, gives a very insoluble salt. The relative proportion of amorphous to crystalline product varies somewhat according to the manner of oxidation. Our experiments indicate that the best yield of the crystalline product was obtained in those cases, in which the oxidation was affected by adding a large quantity of potassium permanganate, allowing it to act for a long time at a low temperature, and finally heating the solution in a water-bath; but in no case did we obtain more than 50 per cent. of this product. On the other hand, adding the permanganate to the solution, and effecting the oxidation quickly, gave the best result for the amorphous product. A large number of oxidation experiments were made, but we describe here only one of them in order to show our method of procedure.

37 grams of the anhydride, $C_{15}H_{10}O_3$, were dissolved in caustic potash, the solution diluted to one liter, and then a solution of 86 grams of permanganate in 1500 cc. water were added in several portions. The temperature of the solution was 29° before the addition, but it gradually rose, and in about 45 minutes it reached its maximum of 50°. After standing an hour and a half, the solution was decolorized, and after further addition of 8 grams permanganate, the solution was heated on the water-bath, when it decolorized on heating several hours. The solution was filtered, the filtrate concentrated to 400 cc., then neutralized with hydrochloric acid, and an excess of a hot concentrated solution of barium chloride added. After standing some hours the precipitate was removed, and the filtrate acidified with hydrochloric acid and extracted with ether. The ether extract was shaken out with a titrated solution of caustic potash, it requiring 14.4 grams caustic potash, which corresponds to 23 grams of acid, assuming it to be a tetrabasic acid with the molecular weight 360. This solution, which did not give a precipitate with barium chloride even after concentration, was evaporated to 100 cc. and used for the following experiments: A portion was acidified, extracted with ether and portions of the viscous acid left on evaporation of the solvent boiled with the carbonates of magnesium, lithium, strontium, calcium and zinc,

but in all cases only soluble amorphous salts were obtained. Another portion of the solution was treated with aqueous silver nitrate, when an almost white, granular precipitate of the silver salt was deposited.

0.6777 gram salt, dried *in vacuo*, first at ordinary temperature, then for one-half hour at 60°, gave 0.3626 gram Ag.

	Theory for $C_{12}H_6(COOAg)$.	Found.
Ag	56.99	53.52

Although the result only approximately agrees with that required by theory, it indicates that the acid is tetrabasic, providing the molecule of the anhydride, $C_{18}H_{10}O_3$, was not split into two molecules in the oxidation.

36 grams of the vacuum-dried silver salt with 70 grams dry ether and 40 grams methyl iodide were mixed in a sealed tube with cooling, and, after the reaction ceased in the cold, the tube was heated for two hours to 100°. On working up the product of the reaction 7 grams of a neutral, and three grams of an acid, oil were obtained. The neutral oil became solid on standing in a vacuum, and was soluble in ether, benzene, chloroform, acetic ester and acid, but not in petroleum ether. It decomposed when an attempt was made to distil it in a vacuum. All attempts to obtain this product in crystalline form were fruitless, but by dissolving it in alcohol, adding some water, and placing the solution in a freezing-mixture of salt and ice, it separated out in a form in which it could be powdered. This operation was repeated twice, and the product analyzed.

0.11051 gram ester gave 0.2514 gram CO_2, and 0.0478 gram H_2O.

	Theory for $C_{10}H_6(COOCH_3)_4$.	Found.
C	62.18	62.05
H	4.66	4.81

This result agrees with the formula for a diphenyltetracarboxylic ester, and to confirm this constitution we isolated the hydrocarbon from which the acid is derived.

A quantity of acid was neutralized with barium hydrate, and the solution evaporated to dryness. The barium salt was intimately mixed with barium hydrate, and the mixture

distilled in a tube, through which a current of hydrogen was passed. The solid hydrocarbon which passed over was crystallized from alcohol, and was shown to be diphenyl.

Although it cannot be regarded as definitely established, the preceding experiments make it probable that both of the products formed in the oxidation of the anhydride, $C_{18}H_{10}O_3$, are diphenyltetracarboxylic acids.

Hydrocarbon from the Anhydride, $C_{18}H_{10}O_3$.

The reduction of the anhydride, through its oxidation product, to diphenyl showed that it must be closely related to this hydrocarbon, and in the expectation that the isolation of the mother-hydrocarbon of the anhydride, and its examination, would give further insight into the nature of the reaction, we turned our investigation in this direction.

Equal weights of the dried barium salt of the acid, $C_{18}H_{10}O_4$, and dehydrated barium hydrate, were quickly heated in a tube, through which a current of hydrogen was passed. A thick oil passed over into the receiver, which was extracted with ether, and the solution shaken out with alkali and dried with calcium chloride. After evaporating the ether a thick oil remained, which weighed about three-fifths as much as the anhydride used. It was fractionated in a vacuum, when almost all of it passed over at 194° (18 mm. pressure, thermometer in vapor). This oil was colored very slightly yellow, but redistillation failed to remove the color.

0.2104 gram oil gave 0.7244 gram CO_2, and 0.1140 gram H_2O.

	Theory for $C_{16}H_{12}$.	Found.
C	93.90	93.90
H	5.79	6.02

The oil has a decided odor of naphthalene, and is readily soluble in glacial acetic acid, but the addition of comparatively little water causes part of the dissolved substance to separate. It is miscible with alcohol only to a moderate extent. The oil did not solidify in a freezing-mixture, and at ordinary pressure it passes over at 326°–327° (corrected 336°–337°).

A molecular weight determination, using glacial acetic acid as solvent, gave 244, while the theory for $C_{16}H_{12}$ is 204.

A comparison of the properties of this hydrocarbon with those given by Möhlau and Berger[1] for α-phenylnaphthalene leave no doubt as to the identity of the two products.

These chemists oxidize their product with potassium permanganate in the presence of caustic soda, to benzoylbenzoic acid, but as we found that this oxidation proceeds slowly, we used chromic anhydride for this purpose. Six grams of oil were dissolved in 50 cc. glacial acetic acid, and 30 grams moist chromic anhydride gradually added in the following manner: One-quarter at first, and the solution slowly heated to 70°, then cooled, and the rest of the chromic anhydride added at once. The solution was heated for three hours at 100°, then the excess of anhydride reduced by addition of alcohol, and the solvent distilled off in a vacuum. The green residue was taken up with water, excess of sulphuric acid added, and the solution extracted with ether. On extracting the ether with caustic potash, and evaporating the solvent, a small amount of a neutral substance, probably an intermediate oxidation product, was left behind. The alkaline solution was then acidified, extracted with ether, and the moist solution left large crystals of pure hydrated benzoylbenzoic acid.

0.1851 gram substance, air-dried, gave 0.4687 gram CO_2, and 0.0840 gram H_2O.

	Theory for C_6H_5—C(OH)$_2C_6H_4$,COOH.	Found.
C	68.85	69.06
H	4.92	5.06

The acid melted at 94°, and agreed in its other properties with benzoylbenzoic acid hydrate. In a vacuum it gradually gave off water, and then melted at 120°–125°. A portion was dried at 100° and analyzed.

0.1436 gram acid gave 0.3922 gram CO_2, and 0.0590 gram H_2O.

	Theory for C_6H_5—CO—C_6H_4—COOH.	Found.
C	74.34	74.49
H	4.42	4.56

As the calcium, barium, and ammonium salts also agree with those of *o*-benzoylbenzoic acid, there can be no doubt of

[1] Ber. d. chem. Ges., **26**, 1198.

the identity of our product with that acid. We also made an experiment to oxidize the anhydride directly with chromic anhydride, and were able to isolate benzoylbenzoic acid from the products of oxidation, but the yield was very unsatisfactory. Diphenyltetracarboxylic acid is apparently not formed in this way.

Theoretical Considerations.

The conversion of the anhydride into α-phenylnaphthalene and into diphenyltetracarboxylic acid, proves its constitution, but the manner of its formation is open to two different constructions. In the first place, one may assume that a molecule of phenylpropiolic-acetic anhydride is added to the unsaturated fatty carbons of a second molecule, in such a manner that one of the orthohydrogen atoms of the nucleus of the first molecule is added to the α-unsaturated carbon in the side chain of the second molecule, and the negative radical remaining unites with the β-unsaturated carbon, thus giving rise to the following constitution :

$$C_6H_5—C—C—CO—O—OCCH_3 + C_6H_5—C—C—CO—O—$$

$$\begin{array}{c} C_6H_5 \\ | \\ OCCH_3 = C_6H_4 \Big\langle \begin{array}{c} C—CH—CO—O—OCCH_3 \\ C—C—CO—O—OCCH_3 \end{array} \end{array} .$$
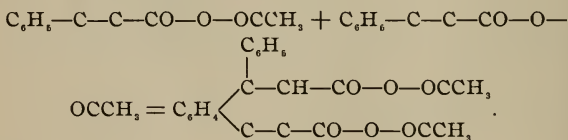
The compound thus formed then undergoes a molecular rearrangement, in which the α-hydrogen of the side chain passes over to the β-carbon of the less saturated side chain, the two α-carbons then saturating each other to form a naphthalene ring :

$$\begin{array}{c} C_6H_5 \\ | \\ C_6H_4 \Big\langle \begin{array}{c} C—CH—COOOCCH_3 \\ C—C—CO—O—OCCH_3 \end{array} = \end{array}$$

$$\begin{array}{c} C_6H_5 \\ | \\ C_6H_4 \Big\langle \begin{array}{c} C — C—CO—O—OCCH_3 \\ CH—C—CO—O—OCCH_3 \end{array} . \end{array}$$
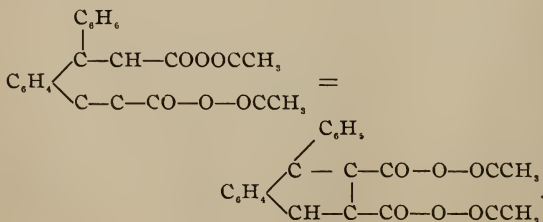
The chain formation is accompanied by the decomposition of the mixed anhydride :

$$C_6H_4 \left\langle \begin{array}{c} \overset{C_6H_5}{\underset{|}{C}} - C - CO - O - OCCH_3 \\ | \\ CH - C - CO - O - OCCH_3 \end{array} \right. =$$

$$C_6H_4 \left\langle \begin{array}{c} \overset{C_6H_5}{\underset{|}{C}} - C - CO \\ | \qquad\quad \rangle O + (CH_3CO)_2O. \\ CH - C - CO \end{array} \right.$$
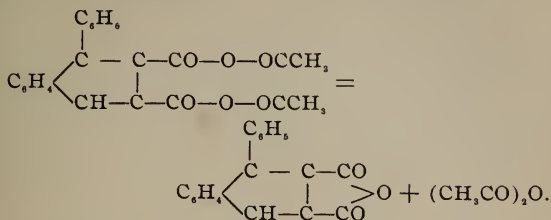
According to the second conception, it may be assumed that an orthohydrogen passes over to the unsaturated β-carbon of the side chain, and this radical then polymerizes with a second molecule of the mixed anhydride :
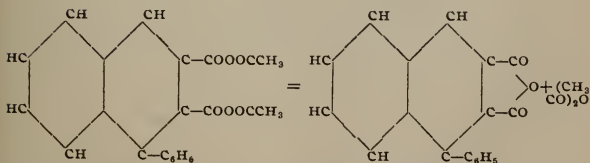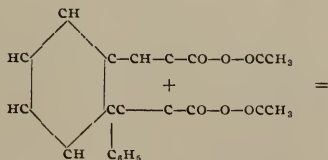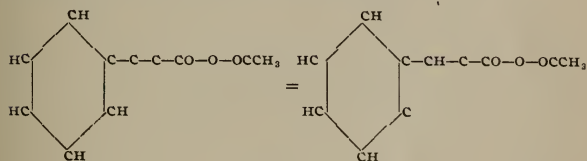
The substance formed by the action of acetic anhydride on phenylpropiolic acid is therefore the anhydride of 1-phenyl-2,3-naphthalenedicarboxylic acid, a constitution with which

all the above-described decompositions of the substance are in accordance. It will be shown farther on that the second is the most probable of these two explanations of its formation. By the action of potassium permanganate in alkaline solution the acid corresponding to the anhydride is converted into diphenyltetracarboxylic acid, and a second acid, apparently isomeric with this substance. The formation of the tetrabasic acid may be represented as follows :

$$+ 9O = \qquad + 2CO_2 + H_2O.$$
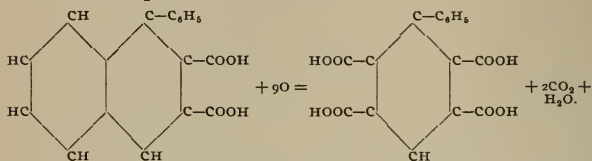
The constitution of the diphenyltetracarboxylic acid therefore follows from that of the naphthalene derivative, and it may be called 1-phenyl-2,3,5,6-benzenetetracarboxylic acid. This constitution agrees with the conversion of the acid into an anhydride, which behavior shows that it contains two pairs of carboxyls, the members of which are in the ortho-position to each other. In regard to the second product of oxidation, it cannot be considered that its constitution as a tetracarboxylic derivate of diphenyl has been conclusively proven ; indeed the formation of a second isomeric acid by oxidation of the anhydride is not foreseen by theory. As the substance is undoubtedly a diphenyl derivative, a further investigation of this product is of interest. The formation of diphenyltetracarboxylic acid is peculiar in view of the oxidation of phenylnaphthalene by the same oxidizing agent,[1] or by chromic acid, to orthobenzoylbenzoic acid. It should be remarked, however, that the oxidation with permanganate was finished in acid solution. The behavior of the α-phenylnaphthalene, obtained by us, towards permanganate in presence of alkali, did not agree with the result obtained by Möhlau and Berger, unless it is that in their case the greater part of the oxidation was done in acid solution. A portion of our hydrocarbon was boiled for a long time, in presence of alkali, without much diminution of oil. It would

[1] Möhlau and Berger: Ber. d. chem. Ges., **26**, 1199.

seem as if there were some connection between the formation of the tetrabasic acid, when the oxidation takes place in presence of alkalies, and of the less acidic benzoylbenzoic acid, when it takes place in acid solution.

A notable difference occurs also in reducing in alkaline and in acid solution, the hydrogen in the first condition attacking the nucleus, while in the second it acts on a carbonyl. When the anhydride is subjected to the action of hydrogen, the reaction proceeds as in the case of phthalic anhydride, reducing the compound to a lactone, $C_{18}H_{12}O_2$:
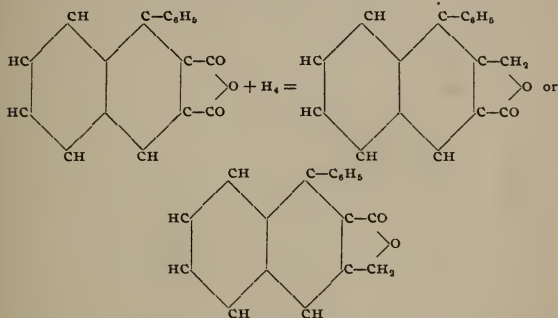
Of these two constitutions the former is the more probable, as the most negative carbonyl should be that nearest to phenyl, and it should be first to be reduced. Hydrogen, in acting on the salt of the dibasic acid, may form isomeric compounds, according to whether it attacks the substituted or unsubstituted nucleus. However, all analogy shows that it would be added to the more negative unsaturated carbons, and it may be considered as reasonably certain that the following equation correctly represents the reaction :
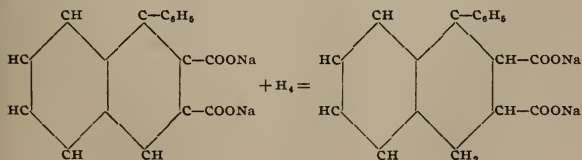
The behavior of the unreduced and reduced acids towards permanganate agrees with this constitution, as it has been found that in the case of aromatic acids the reduction of the nucleus invariably makes the product more susceptible to oxidation.

It is a well-known fact that the replacement of the hydrogen in maleïc anhydride increases the stability of the anhydride, so that certain compounds, as dialkyl- or diphenylmaleïc anhydrides, only exist in anhydride condition, the corresponding acids immediately decomposing into anhydrides and water when they are liberated from their salts. This class of anhydrides have hitherto only been known with fatty acids, or aromatic acids in which the carboxyls entering into the anhydride formation form part of the side chain. We have therefore in 1-phenyl-2,3-naphthalenedicarboxylic anhydride, *the first instance of this spontaneous anhydride formation in an acid, in which the carboxyls are directly connected with the aromatic nucleus*. Owing to the lack of experimental material the influence of the alkyl or phenyl on the facility of anhydride-formation of polybasic aromatic acids, which have the carboxyls joined directly to the nucleus, cannot be as definitely traced as in the fatty series, but that this influence is closely related in both series there can be no doubt. Phthalic acid melts at 203°, losing water at that temperature, and passing over into the anhydride; the introduction of methyl in the meta position to both carboxyls, gives an acid that loses water gradually when heated to 100°,[1] and when methyl is introduced into the ortho position to one of the carboxyls the methylphthalic acid formed goes over into its anhydride at 100°, even in the presence of water.[2] Judging by analogy with the fatty series one should expect that an orthodimethylphthalic acid would spontaneously decompose into anhydride and water, but the acid[3] described as such exists in the free state, and does not lose water more easily than the orthomonomethylphthalic acid.[4] Since phenyl favors anhydride-

[1] Von Niementowski: Monatshefte, **12**, 626.

[2] Young: Ber. d. chem. Ges., **25**, 2107.

[3] Gucci and Cristaldi: Centrbl., **62**, II, 548.

[4] This stability leads one to suspect that the acid may have a different constitution from the one ascribed to it.

formation more than methyl,[1] it is not difficult to understand that our product, which may be considered as derived from phthalic acid by replacing an ortho hydrogen by phenyl and the hydrogen in the meta position to both carboxyls by tetramethylene, should not exist in a free state. There can be no doubt that simpler derivatives of phthalic acid will also show a like behavior.

The synthesis of phenylnaphthalenedicarboxylic anhydride from phenylpropiolic acid is not without analogy, but undoubtedly stands in intimate relation to the formation of the isatropic acids from atropic acid. According to the investigations of Fittig[2] the isatropic acids represent reduced naphthalene derivatives, and their formation may be supposed to take place in a manner exactly similar to the two explanations, which we gave for our substance:

$$2C_6H_5-\underset{\underset{COOH}{|}}{\overset{\overset{|}{|}}{C}}-\overset{|}{C}H_2 = C_6H_4 \underset{\underset{COOH}{C-CH_2}}{\overset{C_6H_5}{\overset{\diagup}{C}\diagdown}}\overset{COOH}{\underset{CH_3}{}} = C_6H_4 \overset{H_5C_6}{\underset{\underset{COOH}{CH-CH_2}}{\overset{\diagup}{C}\diagdown}}\overset{COOH}{\underset{}{CH_2}}$$

or

$$C_6H_4 \overset{\overset{C_6H_5\ COOH}{\diagdown\diagup}}{\underset{\underset{COOH}{C-CH_2}}{\overset{CH_2-CH}{\diagup}}} = C_6H_4 \overset{C_6H_5}{\underset{\underset{COOH}{CH-CH_2}}{\overset{CH_2-CCOOH}{\diagup}}}$$
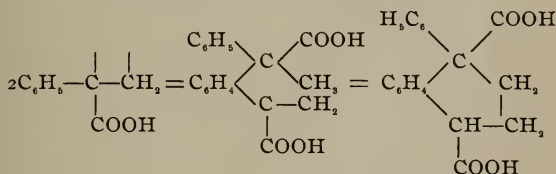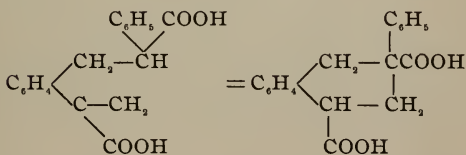
The second of these reactions cannot have taken place, as Fittig proved that the isatropic acids give *o*-benzoylbenzoic by oxidation, and, although it is possible that two molecules of atropic acid unite to form a substance of the constitution represented by the first formula, still it is theoretically very improbable that such a product would easily pass over into the tetrahydronaphthalene derivative, as the hydrogen would

[1] Phenylmaleïc acid loses water with greater ease than does methylmaleïc acid.
[2] Ann. Chem. (Liebig), **206**, 34.

have to leave methyl, and such β-hydrogen shows little tendency to separate from saturated carbon. It is therefore probable that the formation of isatropic acid proceeds by an ortho-hydrogen reducing the adjacent unsaturated carbon of the side chain, and the unstable substance thus formed unites immediately with a second molecule of atropic acid :

$$C_6H_5-\underset{\underset{COOH}{|}}{\overset{|}{C}}-CH_2 = \underset{\underset{COOH}{|}}{\overset{|}{C}_6H_4}-\overset{|}{C}H-\overset{|}{C}H_2$$

$$\underset{\underset{COOH}{|}}{\overset{|}{C}_6H_4}-\overset{|}{C}H-\overset{|}{C}H_2 + C_6H_5-\underset{\underset{COOH}{|}}{\overset{|}{C}}-\overset{|}{C}H_2 = C_6H_4 \overset{\displaystyle C_6H_5}{\underset{\displaystyle CH-CH_2}{\underset{\displaystyle COOH}{\Big\langle}}}\overset{\displaystyle COOH}{\underset{}{C-CH_2}}$$
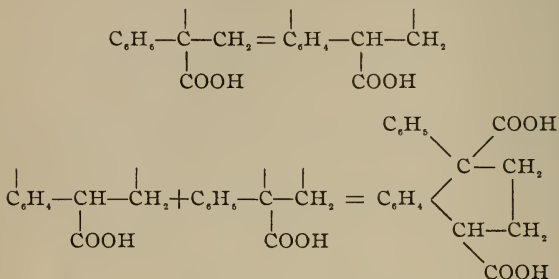
The isatropic acids, considered as reduced naphthalene derivatives, may also be called 1-phenyl-1,4-tetranaphthalenedicarboxylic acids.[1] Chemically related to these acids is tetrahydronaphthalenedicarboxylic acid, which on heating first loses water to form an anhydride, then water and carbon monoxide, passing over into naphthalene. Isatropic acid also loses carbon monoxide and water on heating to form atronic acid, or with concentrated sulphuric acid to form the isomeric isatronic acid. As it is very probable that this decomposition is similar to that of tetrahydronaphthalenedicarboxylic acid, the formation of these acids may be represented as follows :

[1] Fittig (Ann. Chem. (Liebig) **206**, 64) also discussed the possibility of the isatropic acids being tetramethylene derivatives, and showed that such a constitution is not in accordance with the formation of benzoylbenzoic acid by oxidation. Liebermann (Ber. d. chem. Ges., **28**, 138), some years later, without any new experimental material, considered the tetramethylene constitution as possible ; but that this cannot be the case is evident from the results he obtained in the oxidation of the truxillic acids. The experimental analogy, which Fittig stated as wanting at the time of his work, now exists, and there can be no doubt as to the correctness of the reduced naphthalene constitution, a view which is confirmed by the analogy with the phenylpropiolic acid reaction. We should not have considered it necessary to call attention to this error of Liebermann, if it were not that the obvious mistake of considering isatropic and atropic and truxillic and cumamic acids as standing in the same relation to each other has passed over into a text-book (Richter, Organische Chemie, 7te Auflage. II, 275).
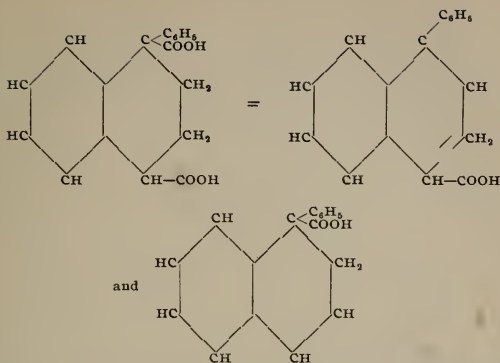
Heated above their melting-points, atronic and isatronic acids give off carbon dioxide, and pass over into the same hydrocarbon which Fittig called atronol. This body is a dihydrophenylnaphthalene, and should possess one of the two constitutions,[1]
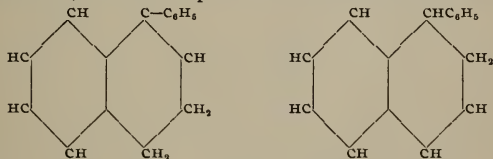
In the decomposition of isatropic acids by sulphuric acid, if the temperature is allowed to rise, a sulphonic acid of a hydrocarbon $C_{16}H_{12}$ is formed. Fittig called the hydrocarbon as atronylene, and suggested for it the following constitutions :
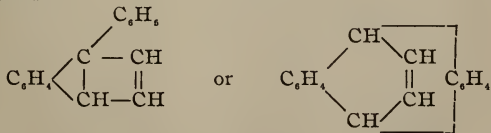
[1] Fittig assigns to atronol the constitution of a 1,4-dihydro-1-phenylnaphthalene. This constitution is not in as close relationship to the atronic acids as those given above, although it is not impossible that such a substance may be formed by molecular rearrangement of the hydrogen in the reduced nucleus. A body having the constitution assigned by Fittig to atronol should be obtained by reduction of α-phenylnaphthalene, and this reaction will be studied.

These interpretations of the reaction are, however, not probable, and there can be little doubt that sulphuric acid acts on isatronic acid in the same manner as it does on isatropic acid, converting it, with the liberation of carbon monoxide and water, into phenylnaphthalene, and the so-called atronylenesulphonic acid is α-phenylnaphthalenesulphonic acid :
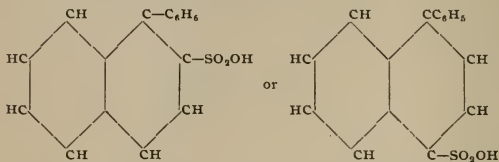
The sodium salt of this sulphonic acid shows a remarkable decomposition, losing sodium hydrate, and being converted readily into a sulphone. This is a reaction which as yet has no precedent in organic chemistry, but is probably due to a peculiar atomic arrangement in space causing the phenyl,[1] or the unsubstituted part of the nucleus, to condense with the sulphonoxyl radical:
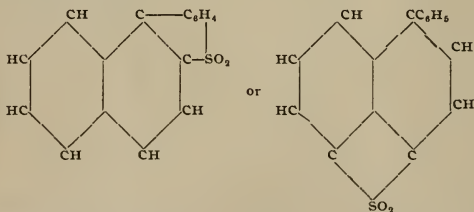
It is evident that the syntheses of naphthalene derivatives from atropic and phenylpropiolic acids are due to reactions essentially analogous in their nature, and as the second of the possible interpretations of the formation of the isatropic acids is theoretically much more probable than that first stated, it is therefore likely that the phenylpropiolic-acid reaction proceeds in a like manner. In these reactions we have a new procedure, by which certain phenyl derivatives with unsaturated side chains, undergo polymerization with union of carbon atoms to form naphthalene derivatives.

TUFTS COLLEGE, November 1897.

[1] The behavior of α-phenylnaphthalene towards sulphuric acid will be examined in the hope of confirming this view. It is possible, however, that in this case an isomeric sulphonic acid may be formed.

THE RELATION OF THE TASTE OF ACIDS TO THEIR DEGREE OF DISSOCIATION.

By Theodore William Richards.

Since no systematic attempt appears to have been made to determine acids quantitatively by means of the sense of taste alone, it seemed worth while to carry out the following series of experiments with this idea in view.[1] The peculiar sourness which is distinctive of acids is probably to be referred to the hydrogen ion, which also is distinctive of them, and it becomes a question of no small interest to determine how closely the taste corresponds to the degree of dissociation.

The sense in question is well known to be rather an uncertain one, depending upon the habits and physical condition of its possessor, so that an experimenter could hardly expect to obtain absolute results from its use. On the other hand, relative taste, determined by alternately tasting two solutions, might well furnish some clue as to the relative strength of these solutions.

The water used in the experiments recorded below was distilled in a platinum still over alkaline permanganate, the first portions of the distillate being rejected. For the final experiments this water was redistilled; in this way an unusually tasteless liquid may be obtained. The solutions of acids, alkalies and salts were carefully made of pure materials. The test was accomplished by simply taking a small mouthful (five cubic centimeters) of the liquid in question, (which is advantageously warmed beforehand to 40°) and allowing this liquid to remain upon the tongue for a few seconds until a constant intensity of taste is secured. A few of the individual experiments are recorded below in order to define the method, but most of them are merely indicated in the conclusions.

(1) To four several portions of water, each measuring 10 cc., were added respectively 0.05, 0.10, 0.20 and 0.30 cc. of decinormal hydrochloric acid. The first of these solutions

[1] Dr. Squibb has used this physiological method upon cocaine with good results. (Ephemeris of Materia Medica, Etc., Brooklyn, N. Y., Vol. III., No. I, p. 918, 1887.) My attention was called to this interesting work after the present paper was written, and I know of no similar investigation.

remained unchanged in taste, the second became faintly acid, and the others very distinctly so.

(2) In order to test the degree of accuracy attainable in this way, a number of beakers containing dilute acid were "shuffled" so that the identity of each was lost, and the attempt was then made to arrange them according to strength by means of the taste alone. Small inconspicuous labels showed finally how successful the attempt had been. In the first trial, four beakers, each containing 30 cc. of water, were acidified by adding 0.2, 0.4, 0.6 and 0.8 cc. of deci-normal hydrochloric acid. These were arranged by taste without great deliberation in their proper order, showing that the method is capable of an accuracy of twenty-five per cent., even with a comparatively unpractised tongue.

(3) Another similar trial was made with similar amounts of water containing 0.3, 0.4, 0.5 and 0.6 cc. of decinormal acid respectively. After repeated tasting and much deliberation these were arranged in the order 1, 2, 4, 3; thus my success with the method did not go beyond 20 per cent., although the limit might unquestionably be reduced by practice.

Similar experiments with sulphuric, nitric, and hydrobromic acids showed that the sensitiveness in these cases is about the same—an acid of the concentration of somewhat less than $\frac{1}{1000}$ normal, representing the limit of possible detection as indicated by my sense of taste. This is a very weak solution, containing less than a milligram of hydrogen ions in a litre.

It is, of course, possible that a part of this taste might be due to the negative ion. Further light upon this point is obviously to be obtained by neutralizing the acid with potash or soda. It was found in this way that an acid liquid which tasted distinctly sour became absolutely tasteless upon neutralization; indeed, a centinormal solution of potassium chloride has less taste than a millinormal solution of acid. According to the dissociation hypothesis, the hydrogen ions have been removed by the neutralization, and we are now tasting potassium and chlorine ions, which are either not very strong in taste, or else have the peculiar property of nearly eliminating

one another's taste by mixture. Since most properties of solutions are additive, and we cannot well conceive of a *minus* taste (except such a subtraction from the taste as might be caused by a partial paralysis of the nerves, owing to some very powerful excitement), the former alternative seems to be the most natural one; hence we may believe that neither potassium nor chlorine ions possess as strong a taste as those of hydrogen.

It becomes now a matter of interest to compare these results with those given by very dilute solutions of less ionized acids. Tartaric acid thus diluted, tasted somewhat less sour than a corresponding solution of the mineral acids, citric acid was still less sour, and acetic acid was the least sour of all. While qualitatively these observations agree with those which we should expect to make, the quantitative agreement is less satisfactory. Acetic acid, for instance, seemed to taste at least as strong as hydrochloric acid of one-third its concentration, whereas at a concentration of $\frac{1}{318}$ normal, Kohlrausch's experiments upon its electrolytic conductivity show that only about one-fourteenth of the acid is dissociated.[1] The reason for this discrepancy is not evident, unless the act of tasting removes the dissociated part of the acid and so leaves room for further dissociation, or unless the undissociated acid possesses a taste resembling that of the hydrogen ions, but weaker. Both of these hypotheses carry one too far into physiological chemistry to receive treatment here.

Somewhat more satisfactory were the results of mass action upon the taste. The addition of small amounts of potassic chloride to very dilute solutions of hydrochloric acid produced no appreciable effect upon the taste, while the sourness of acetic acid was noticeably diminished, and that of hydrochloric acid was almost destroyed by adding similar amounts of potassic or sodic acetates. These phenomena are qualitatively in accord with the dissociation hypothesis and the mass law, which tell us that in such a reaction as

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
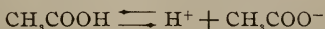
[1] At 18°, when $v = 167$ $\mu = 17.0$
    " $v = 500$ $\mu = 28.3$ Weid. Ann., **26**, 161, (1885).
    " $v = \infty$ $\mu = 318.4$

the addition of a large proportion of acetic ions from the almost wholly dissociated sodic acetate is capable of forcing the reaction backwards and destroying the hydrogen ions. The case is of course analogous to the effect of salts in modifying the catalytic action of acids upon cane-sugar and esters, as measured by Ostwald,[1] Arrhenius,[2] Spohr,[3] Trevor,[4] Palmaer,[5] and others. We should expect, however, to find the taste of the acetic acid wholly destroyed by the addition of sodic acetate, because the acid's power of inverting sugar is so much diminished thereby ; and the fact that some acid taste remains is only to be accounted for by some such hypothesis as those given above. The fact that the taste of hydrochloric acid is diminished much more than that of acetic acid by the addition of sodic acetate is not inconsistent with these hypotheses ; for acetic acid, whether wholly or partly undissociated, has been shown to be much less sour than hydrochloric acid ; and acetic acid is undoubtedly formed in this case.

A common application of these principles is to be found in the preparation of the much-used "soda water" or "mineral water" of commerce. Unless a small amount of sodic carbonate is added during its preparation, the effervescent solution is so sour as to be unpleasant to some tastes. This sourness may sometimes have been augmented by a stronger acid carried over in the process of careless preparation ; but the fact that it exists in some degree, even in carefully prepared carbonic acid water, was shown by experiment in the laboratory. In any case the sourness is removed by sodic bicarbonate, and the hypothetical explanation is similar to that given above. The following equilibrium is usually assumed to exist in the solution of carbonic acid :

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$
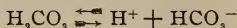
The acid is, however, only very slightly dissociated. Hydric sodic carbonate, on the other hand, is probably largely dissociated into Na^+ and HCO_3^-, and when this salt is added these latter ions force back the already very slight dissociation of

[1] J. prakt. Chem. (1883), **28,** 449; also (1885) **31,** 307.
[2] Ztschr. physikal. Chem., **4,** 226.   [3] J. prakt. Chem. (1885), **32,** 32.
[4] Ztschr. physikal.Chem., **10,** 321.   [5] *Ibid*, **22,** 492.

the carbonic acid, rendering the solution pleasant and soft to the taste by removing some of the hydrogen ions.

Since sodic chloride was found to possess a taste so much feebler than that of hydrochloric acid, it is evident that the sense of taste might form a fairly sensitive indicator of the end-point of an acidimetric reaction. It is possible easily to detect sourness in a millinormal solution of acid, hence in working with decinormal solutions of acids and alkalies we ought to be able to determine the end-point to within 1 or 2 per cent.

Accordingly several titrations were made with exactly decinormal solutions of hydrochloric acid and sodic hydroxide, the liquid being tasted with a glass rod until the end-point was nearly reached, when small mouthfuls were tasted. The alkalinity of saliva is insufficient to make any essential difference in the results. If large amounts of liquid are removed, it is obviously necessary to allow for the acid or alkali thus taken out; but this correction may be reduced to a very small amount by the use of large quantities of the original solutions.

The best results were obtained by adding slightly too much acid, and then adding alkali until the sour taste just disappeared. The figures are given below—the first and second columns containing the number of cubic centimeters of acid and alkali respectively, and the third the percentage of acid found.

Acidimetric Titration.

Cc. of acid taken.	Cc. of alkali taken.	Per cent. of acid found.
7.00	6.99	99.9
10.73	10.67	99.4
7.21	7.15	99.1
14.96	14.99	100.2
14.44	14.59	100.9
	Average	99.9

The accuracy of these results, which were obtained in an unprejudiced fashion, is somewhat astounding. Evidently, in the course of the few experiments described here, the sense of taste had been noticeably sharpened. To what limit this sensitiveness might be carried, it is hard to predict; but already

the method of analysis had assumed a degree of accuracy exceeding some which are seriously applied as quantitatively useful.

Efforts were made also to analyze the taste produced by weak currents of electricity, as well as the effect of sugars in mitigating the unpleasantness of great acidity of taste, but the complex physiological relations involved in these and similar cases led to an unsatisfactory outcome.

The results of this paper, although they are only qualitatively consistent with the theory of dissociation, nevertheless show that the sense of taste might be used more precisely in the laboratory than is usually believed.

CAMBRIDGE, December 12, 1897.

NOTE ON FEHLING'S SOLUTION.

BY J. BISHOP TINGLE.

M. Z. Jovitschitsch has recently shown[1] that alkaline copper solution, freshly prepared according to Fehling's directions, deposits cuprous oxide either at the ordinary temperature or when heated, if it has been partially neutralized with sulphuric acid, hydrochloric acid, or nitric acid. This result is ascribed to decomposition of the tartrates present in the liquid. It is well known that Fehling's solution slowly undergoes spontaneous decomposition, and the instability of tartaric acid in aqueous solution on exposure to light has been pointed out by W. Seekamp,[2] whilst its oxidation in presence of iron and alkali has been studied by Fenton.[3] Purdy, in his work on "Urine Analysis,"[4] advises, for the determination of dextrose, the use of a solution composed of copper sulphate, potassium hydrate, glycerol, and ammonium hydrate. Since glycerol is much more stable than tartaric acid, it appeared worth while, in view of the intrinsic importance of the subject, to ascertain whether this solution was also affected by the presence of mineral acids. Specimens treated in the manner described by Jovitschitsch, both at the ordinary tempera-

[1] Ber. d. chem. Ges. (1897), **33**, 2431.
[2] Ann. Chem. (Liebig), **278**, 373 ; also R. Otto: Ber. d. chem. Ges. (1894), **27**, 799.
[3] J. Chem. Soc. (London), 1894, 890 ; 1896, 546 ; 1897, 375.
[4] Practical Urine Analysis (3d Edition). F. A. Davis Co., Philadelphia, 1896.

ture and at the boiling-point, gave no sign of reduction. The liquid is very sensitive towards phenylhydrazine, and is readily reduced by lactose, and maltose on heating. The reduction is shown by the weakening or complete discharge of the blue color, and not by the production of a precipitate as in the case of the ordinary Fehling's solution. Purdy's formula for the preparation of the liquid is as follows : Crystallized copper sulphate (4.742 grams) is dissolved in water (200 cc.), and glycerol (38 cc.) ; potassium hydroxide (23.5 grams) is dissolved in water (200 cc.), the solutions are mixed, ammonium hydrate (sp. gr. 0.9, 450 cc.) is added together with sufficient water to make 1 litre. Of this solution 35 cc. are equivalent to 0.02 gram dextrose. In determining dextrose 35 cc. of the copper solution are diluted with about 2 volumes of water, boiled, and the sugar solution added drop by drop from a burette until the blue color is discharged. The copper solution may be kept for an indefinitely long time without undergoing change.

LEWIS INSTITUTE, CHICAGO, ILL.

ACTION OF THE ANHYDRIDE OF ORTHOSULPHO-BENZOIC ACID ON DIMETHYL- AND ON DIETHYLANILINE.

BY M. D. SOHON.

When the anhydride was mixed with dimethylaniline and heated, a green color was developed at about 90°, but the reaction did not proceed to any extent. A similar color was obtained by boiling the mixture in benzene solution for several days. In neither case could the products be separated. Dimethylaniline (2 mols.) was mixed with the anhydride (1 mol.), phosphorus oxychloride added in equal amount, and the mass gently heated on the water-bath, for a short time. Quite an energetic action ensued ; the resulting product was boiled with water, when a black tarry mass separated. After cooling, the green supernatant liquid was decanted, and the washing repeated until the wash-water was blue, and the mass solidified on cooling. The wash-waters were examined and found to contain only phosphorus, hydrochloric, and sulpho-

benzoic acids, with some of the green material, the chief product.

Dimethylanilinesulphonphthaleïn,

$$C \begin{cases} C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \\ C_6H_4SO_2 \\ O\text{---}\end{cases} = C_{22}H_{24}N_2SO_3$$
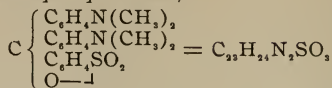
thus obtained is a blue-black, brittle mass, appearing bright blue in fine powder. Sparingly soluble in cold water, more soluble in hot water, with a bright blue color. Excess of the sulphonphthaleïn in hot water formed a tarry mass which solidified on cooling if pure. It is soluble in alcohol, the solution being precipitated by ether, in which it is insoluble. It is also insoluble in benzene, ligroïn, and chloroform. Analyses gave the following results :

0.4000 gram gave 0.2254 gram $BaSO_4$, equivalent to 7.73 per cent. sulphur.

0.3112 gram gave 0.1781 gram $BaSO_4$, equivalent to 7.80 per cent. sulphur.

0.4121 gram gave 0.0277 gram N, equivalent to 6.72 per cent. nitrogen.

The formula $C_{22}H_{24}N_2SO_3$ requires 7.84 per cent. sulphur and 6.82 per cent. nitrogen.

The aqueous solution of the sulphonphthaleïn dyes silk or wool bright blue. It is more soluble in acids than in water ; in dilute acid it dissolves with a green color, becoming yellow on addition of excess of acid. Apparently an unstable salt is formed. On evaporation of the hydrochloric acid solution to dryness, the residue was found to be free from chlorine, and acted like the original material. Neither could any decomposition be effected by boiling with acid. On heating with concentrated hydrochloric acid in a sealed tube, one and a half hours at 180°, decomposition was effected ; the material was charred and nothing definite could be obtained.

Phosphorus pentachloride did not act upon it. Heated in a closed tube at 180° the result was similar to that with hydrochloric acid.

Reducing agents failed to act upon the sulphonphthaleïn,

tin, granulated zinc and zinc dust in acid and in alkaline solution, and also sulphites were tried.

The acid or neutral solution, on addition of excess of alkali, becomes pink ; the product could not be separated. On removal of the excess of alkali it regained its original color. Nor could change be effected by long boiling. On fusion with potassium hydroxide, empyreumatic odors were evolved and only a carbonaceous residue obtained.

Acetic anhydride did not act upon it, nor bromine in glacial acetic acid solution.

Diethylanilinesulphonphthaleïn,

$$C\begin{cases} C_6H_4N(C_2H_5)_2 \\ C_6H_4N(C_2H_5)_2 \\ C_6H_4SO_2 \\ O\text{---} \end{cases} (= C_{27}H_{32}N_2SO_3),$$
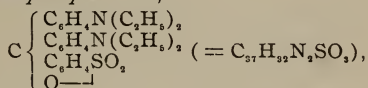
prepared in the same manner as the dimethylaniline compound, is similar in its properties. The color was more green.

0.2663 gram gave 0.1315 gram $BaSO_4$, equivalent to 6.78 per cent. sulphur.

0.3112 gram gave 0.1539 gram $BaSO_4$, equivalent to 6.79 per cent. sulphur.

0.1517 gram gave 0.00948 gram N, equivalent to 6.25 per cent.

The formula $C_{27}H_{32}N_2SO_3$ requires 6.89 per cent. sulphur and 6.02 per cent. nitrogen.

THE MOLECULAR WEIGHT OF LACTIMIDE.

By G. M. Richardson and Maxwell Adams.

The α-oxy acids yield neutral anhydrides. In the case of glycolic acid,[1] lactic acid,[2] and α-oxybutyric acid,[3] it has been shown that this dehydration takes place between two molecules of the acid thus :

$$RCH\begin{matrix}O\text{ H}\quad HO\text{ CO}\\ \diagup\quad\quad\quad\diagdown\\ CO\text{ OH}\quad H\quad O\end{matrix}CHR = RCH\begin{matrix}O\text{---}OC\\ \diagup\quad\quad\diagdown\\ CO\text{---}O\end{matrix}CHR + 2H_2O.$$
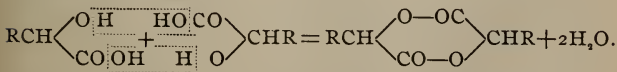
[1] Ber. d. chem. Ges., **26**, 262. [2] *Ibid*, **7**, 753 ; and **26**, 263 and 560.

[3] *Ibid*, **26**, 264.

Anhydrides of the higher α-hydroxy acids have not been obtained.

The β-oxy acids lose water and are converted into unsaturated acids :

$$RCHOHCH_2COOH = RCH\!=\!CHCOOH + H_2O.$$
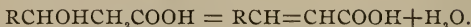
The γ- and δ-oxy acids lose water when set free from their salts :

$$R\!-\!CHOHCH_2CH_2COOH = RCH\!-\!CH_2CH_2CO + H_2O$$
$$\underset{\raise2pt\hbox{$\llcorner O\!-\!-\!-\!-\!-\!\lrcorner$}}{}$$

and

$$R\!-\!CHOHCH_2CH_2CH_3COOH = RCH\!-\!CH_2CH_2CH_2CO + H_2O$$
$$\underset{\raise2pt\hbox{$\llcorner O\!-\!-\!-\!-\!-\!-\!\lrcorner$}}{}$$
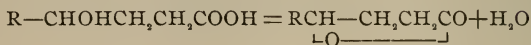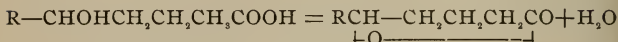
a reaction which finds a ready explanation when the stereochemical relations of the carbon atoms are considered.

The amido acids also yield neutral anhydrides, apparently in a manner analogous to the oxy acids.

Amidoacetic acid and α-amidopropionic acid both give neutral anhydrides. β-Amidopropionic acid when heated gives acrylic acid and ammonia:

$$CH_2NH_2CH_2COOH = CH_2CHCOOH + NH_3.$$
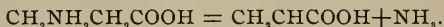
The γ- and δ-amido acids readily lose water forming the lactames

$$CH_2NH_2CH_2CH_2COOH = CH_2CH_2CH_2 + H_2O$$
$$\qquad\qquad\qquad\qquad\quad NH\!-\!\!-\!\!-CO$$
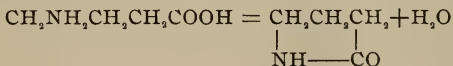
This analogy between the amido acids and the oxy acids suggests that since the dehydration in the α-oxy acids takes place between two molecules of acid, the dehydration in the α-amido acids also takes place between two molecules.

Curtius[1] attempted to determine the vapor-density of the anhydride of amidoacetic acid in order to decide whether its formula was CH_2NHCO or $(CH_2NHCO)_2$, but without results. Nevertheless he concluded that it must have the doubled formula on account of its high melting-point and its indisposition to take up water and pass back into the amidoacetic acid. Later Curtius and Schultz[1] determined the molecular weight of the anhydride by the freezing-point method and found

[1] Ber. d. chem. Ges., **16**, 755.

the doubled formula to be the correct one. They give $CH_2\langle\begin{smallmatrix}NH-CO\\CO-NH\end{smallmatrix}\rangle CH_2$ as the structural formula.
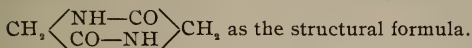
The only other anhydride of this class thus far described is the anhydride of α-amidopropionic acid or *lactimide* described by Pren.[2] Pren gives to this the formula $CH_3CH\langle\begin{smallmatrix}NH\\|\\CO\end{smallmatrix}$, and this is the formula ascribed to the substance in the chemical literature.

From stereochemical considerations, and by analogy to the oxy acids and especially by analogy to the anhydride of amidoacetic acid, it seems probable that the lactimide of Pren should have the doubled formula and be written

$$CH_3CH\langle\begin{smallmatrix}NH-CO\\CO-NH\end{smallmatrix}\rangle CHCH_3.$$
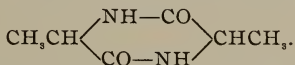
To test this point experimentally the authors prepared lactimide according to the directions of Pren, and determined its molecular weight by the lowering of the freezing-point of its acetic acid solution. The results show the doubled formula $(CH_3CHNHCO)_2$ to be the correct one.

α-Amidopropionic acid (alanin) was prepared from aldehyde ammonia by the following transformations:

$$CH_3C\langle\begin{smallmatrix}H\\NH_2\\OH\end{smallmatrix} + HCN = CH_3C\langle\begin{smallmatrix}H\\NH_2\\CN\end{smallmatrix} + H_2O.$$

Aldehyde ammonia.

$$CH_3C\langle\begin{smallmatrix}H\\NH_2\\CN\end{smallmatrix} + 2H_2O + HCl = CH_3C\langle\begin{smallmatrix}H\\NH_2\\COOH\end{smallmatrix} + NH_4Cl.$$
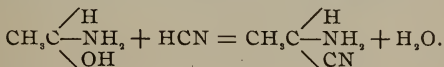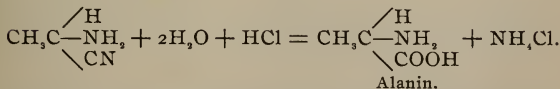
Alanin.

Aldehyde ammonia was prepared in the usual manner and dried. A solution of hydrocyanic acid of known strength was prepared by distilling potassium ferrocyanide with sulphuric acid and passing the hydrocyanic acid into distilled water.

The strength of the solution thus formed was determined by saturating 10 cc. of this solution with potassium hydroxide and titrating with standard solution of silver nitrate.

[1] Ber. d. chem. Ges., **23**, 3041. [2] Ann Chem. (Liebig), **134**, 372.

The aldehyde ammonia was dissolved in water and hydrocyanic acid added in the proportions indicated by the equation. To this was added slightly more hydrochloric acid than the equation indicates, and the whole was evaporated until ammonium chloride began to crystallize out. After cooling, the ammonium chloride was filtered out, and washed with a little water; the filtrate, which contains the alanin, was boiled with lead hydroxide to destroy the ammonium salt left in solution, and finally the lead removed from the solution with hydrogen sulphide, and the alanin crystallized from the filtrate.

The dried alanin was placed in a combustion-tube, and dry hydrochloric acid gas passed over it for three hours while it was kept at a temperature of 180° to 200° C. The tarry residue remaining in the tube was boiled with lead hydroxide to free it from hydrochloric acid and any ammonium chloride that might remain. The lead was then removed with hydrogen sulphide, and the lactimide crystallized from the solution. In this manner was obtained a very small yield (about 0.5 per cent. of the theoretical yield) of needle crystals which melt at 271° (uncorrected) and sublime at about their melting-point with slight decomposition.

The substance is extremely soluble in water, soluble with difficulty in glacial acetic acid, and insoluble in absolute alcohol. Pren[1] reports that lactimide is easily soluble in alcohol. The analytical results are given below:

	Found.	Calculated for $CH_3CHNHCO$.
C	50.4	50.70
H	7.2	7.04
N	...	19.72
O	...	22.54

A molecular weight determination by Beckmann's[1] freezing-point method in acetic acid solutions gave the following results:

Weight of acetic acid used as solvent, 20.5473 grams.
Weight of lactimide dissolved,   0.1549   "

[1] Ann. Chem. (Liebig), **134**, 373.

Freezing-point of pure solvent.	Freezing-point of solution.
2.442	2.236
2.440	2.225
2.442	2.225
2.439	....
Mean, 2.441	2.229

Lowering of the freezing-point, 0.212°.

The molecular lowering of the freezing-point for substances dissolved in acetic acid is 38.8. Hence the molecular weight of lactimide is

$$\text{Molecular weight} = \frac{38.8 \times 0.1549 \times 100}{0.212 \times 20.5473} = 137.9.$$

The molecular weight of the formula $CH_3CHNHCO$ is 71, and for the doubled formula $(CH_3CHNHCO)_2$, the molecular weight is 142.

The results of these experiments show that the second formula is undoubtedly the true one.

STANFORD UNIVERSITY, CAL.,
November 18, 1897.

THE ACTION OF SODIUM ETHYLATE UPON α, β-DIBROMHYDROCINNAMIC ESTER, CITRA-DIBROMPYROTARTARIC ESTER, AND α, β-DIBROMPROPIONIC ESTER.[1]

BY VIRGIL L. LEIGHTON.

The action of sodium ethylate in alcoholic solution upon solid dibromsuccinic ester had been studied by a number of chemists, but owing to the incompleteness and contradictory nature of the results, the subject remained in an unsatisfactory state until recently investigated by Michael and Bucher.[2] It was for the purpose of extending these observations to other similar compounds that the present work was undertaken. The result of the study of dibromsuccinic ester is as follows :

By the action of one molecule of sodium ethylate in alcoholic solution upon sodium succinate, Mulder and Hamberger[3] obtained sodium bromethoxysuccinate, which tested again

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[1] The work described in the following pages comprises part of a thesis presented at Tufts College, for the degree of Doctor of Philosophy.

[2] Ber. d. chem. Ges., **28**, 2512; **29**, 1792.   [3] Rec. d. trav. chim., **1**, 154.

with sodium ethylate did not give a compound free from bromine as was expected.

Mulder and Wellmann[1] report as the result of the action of potassium ethylate (equal molecules) upon dibromsuccinic ester, bromfumaric or brommaleïc ester. By treatment with two molecules a compound was obtained free from bromine, but, although a number of analyses were made, they were so unsatisfactory that the identity of the product could not be established with certainty.

Pum[2] obtained as the result of the action of equal molecules of sodium ethylate on dibromsuccinic ester, brommaleïc ester, and of two molecules of sodium ethylate to one of ester, acetylenedicarboxylic ester.

Michael and Maisch[3] have shown that the properties and boiling-point of the supposed acetylenedicarboxylic ester obtained by Pum do not agree with those of that compound, and that a compound free from bromine is not obtained by using the theoretical amount of sodium ethylate ; but by using an excess of ten per cent. a substance is obtained, which was apparently identical with that of Pum, and which was shown by analysis to be diethoxysuccinic ester.

In a second paper,[4] Pum repeated his former experiments, and stated that he obtained as the product of the action of two molecules of sodium ethylate upon dibromsuccinic ester, a mixture of acetylenedicarboxylic ester and ethoxymaleïc ester, the first ester in relatively small proportion, the acids of which he was able to separate.

Finally, Michael and Bucher[5] have shown that in this reaction an excess of sodium ethylate gives two products, ethoxyfumaric ester (20 per cent.) and unsymmetrical diethoxysuccinic ester (80 per cent.), and that acetylene dicarboxylic ester is not formed even when equal molecules of reagents are used ; but the proportions formed of the above esters are reversed. They have also obtained the same products by treating acetylenedicarboxylic ester with sodium ethylate.

The action of sodium ethylate in alcoholic solution has been studied upon a few other similar compounds, namely,

1 Rec. d. trav. chim., **7**, 334. 2 Monat. f. Chem., **9**, 446.
8 J. prakt. Chem., **46**, 233. 4 Monat. f. Chem., **14**, 491.
5 Ber. d. chem. Ges., **28**, 2512 ; **29**, 1792.

the dibromide of isoeugenol ethyl and methyl ether;[1] anethol dibromide, isosafrol dibromide, and the dibromide of isoeugenol ethyl ether;[2] dibromide of isoeugenol ethyl ether;[3] anethol dibromide and monobromanethol dibromide.[4]

The authors agree that the final product obtained by the action of two molecules of sodium ethylate is a ketone of the following general formula $R.COCH_2CH_3$. This result was explained by Wallach and Pond by supposing that the first action of the sodium ethylate was to split off hydrobromic acid, the ethoxyl radical being then substituted for the second atom of bromine. The product thus formed in contact with water (it was distilled with steam) undergoes hydrolysis, forming an unsaturated carbinol, which being unstable is converted into the ketone. The whole reaction may be represented as follows :

$R,CHBrCHBrCH_3 — HBr = R,CBrCHCH_3$;
$R,CBrCHCH_3 + NaOC_2H_5 = R,C(OC_2H_5)CHCH_3 + NaBr$;
$R,C(OC_2H_5)CHCH_3 + H_2O = R,C(OH)CHCH_3 + C_2H_5OH$;
$R,C(OH)CHCH_3 \quad \longrightarrow \quad R,COCH_2CH_3$.
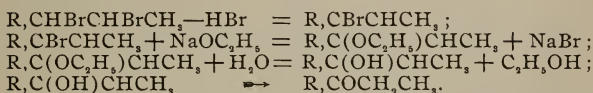
By allowing one molecule of sodium ethylate to act upon ethylisoeugenol dibromide, Hell and Portmann[5] obtained ethoxyethylisoeugenol bromide,

$$C_6H_5(OCH_3)(OC_2H_5)CH(OC_2H_5)CHBrCH_3,$$
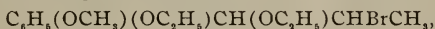
which, when heated, or distilled under 15 mm. pressure, loses alcohol and yields the compound

$$C_6H_5(OCH_3)(OC_2H_5)CHCBrCH_3.$$
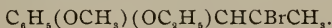
The authors conclude, therefore, that the first action is not to split off hydrobromic acid, but that the bromine atom in the α-position to the benzene ring is first substituted by the ethoxyl radical, then hydrobromic acid splits off, and subsequent hydrolysis gives the ketone thus:

$R,CHBrCHBrCH_3 + NaOC_2H_5 = R,CH(OC_2H_5)CHBrCH_3 + NaBr$
$R,CH(OC_2H_5)CHBrCH_3 — HBr = R,C(OC_2H_5)CHCH_3$
$R,C(OC_2H_5)CHCH_3 + H_2O = R,C(OH)CHCH_3 + C_2H_5OH$
$R,C(OH)CHCH_3 = R,COCH_2CH_3$
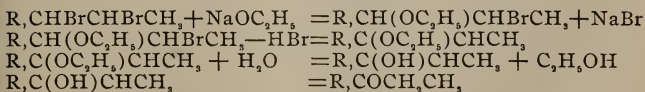
[1] Hell and Portmann : Ber. d. chem. Ges., **28**, 2088.
[2] Wallach and Pond : *Ibid.*, **28**, 2714. [3] Hell and Portmann : *Ibid.*, **29**, 676.
[4] Hell and Hollenberg : *Ibid.*, **29**, 682. [5] *Ibid.*, **29**, 676.

The Action of Sodium Ethylate upon α,β-*Dibromhydrocinnamic Ester.*

The α,β-dibromhydrocinnamic ester used in the following experiments was prepared from cinnamic acid by first converting it into the ester, which was then dissolved in an equal volume of carbon tetrachloride, and the calculated amount of bromine added slowly from a drop funnel in the sunlight, the mixture being kept cool by a bath of ice-water. The carbon tetrachloride was allowed to evaporate, at first spontaneously, then in a vacuum, and finally the remaining oil was sucked out with a pump, and the product washed with a little absolute alcohol and dried. It melted at 67°–68°.

To 10 grams of dibromhydrocinnamic ester suspended in an equal weight of absolute alcohol was added drop by drop a solution of sodium ethylate, made by dissolving 1.5 grams of sodium (theory for two molecules 1.37 grams) in 20 grams of absolute alcohol, the temperature being kept below 6°. Sodium bromide began to separate immediately. After standing six days, it remained alkaline to litmus. It was then saturated with carbon dioxide, the sodium bromide and carbonate separated by filtration and the excess of alcohol distilled off in a vacuum upon the water-bath. A little water was then added to the residue, the supernatant oil separated, shaken out with a solution of sodium carbonate, and dried over calcium chloride. The product contained considerable bromine (detected by the cupric oxide test) from which repeated distillation failed to free it entirely.

To get a product free from bromine 10 grams of the dibromhydrocinnamic ester, treated as before with ten per cent. excess of sodium ethylate, was allowed to stand three days at the ordinary temperature, then boiled two and a half hours on the water-bath. The solution was then neutral, so that 0.15 gram more sodium dissolved in alcohol was added and the solution again boiled two hours. It then remained strongly alkaline. The product worked up as before gave on distillation an oil free from bromine.

This experiment, repeated with 73 grams of dibromhydrocinnamic ester, gave 47 grams of crude product free from bro-

mine. Three grams of phenylpropiolic acid, which crystallized
from hot water in characteristic crystals, melting at 136°, was
obtained from the sodium carbonate solution by acidulating
with sulphuric acid and extracting with ether.

The neutral oil was repeatedly fractioned (with beads) in
a vacuum and finally two products were obtained, one boiling
at 146°–148° at 10 mm. pressure (metal bath 180°), and a
much larger portion boiling at 154°–155° at 9 mm. pressure
(bath 185°). The former product will be described later;
the latter gave the following results on analysis:

0.2141 gram of substance gave 0.554 gram of carbon dioxide
and 0.142 gram of water.

	Calculated for ethoxycinnamic ester.	Found.
C	70.80	70.56
H	7.30	7.38

It was therefore ethoxycinnamic ester.

β-Ethoxycinnamic Acid.

The ethoxycinnamic ester obtained as above was saponified
very slowly by a dilute solution of caustic potash at ordinary
temperature. It was therefore boiled with a very slight
excess of a four per cent. aqueous solution of caustic potash,
in a flask with a return-condenser. After complete solution,
which required about one and a half hours, it was acidulated
with sulphuric acid, when nearly pure ethoxycinnamic acid
was precipitated as a voluminous, white crystalline solid,
which, dried in a vacuum over sulphuric acid, melted
at 158°–160° with decomposition. From carbon tetrachloride
it crystallized in thin, transparent, well-formed crystals, which,
dried over sulphuric acid in a vacuum, melted with decomposition at 164°–165°, and gave the following analytical results :

0.255 gram of substance gave 0.642 gram of carbon dioxide,
and 0.1455 gram of water.

	Calculated for ethoxycinnamic acid.	Found.
C	68.73	68.65
H	6.26	6.38

The ester, dissolved in a little alcohol, was treated with
concentrated hydrochloric acid (sp. gr. 1.2), and evaporated

in a vacuum over sulphuric acid and caustic soda. The residue was again treated with hydrochloric acid, evaporated, and this process repeated until the saponification seemed complete. At the end of the operation the characteristic odor of acetophenone was noticeable. The residue, a white crystalline solid, was dissolved in hot benzene and a few drops of ligroïn added, when benzoylacetic acid separated out in well-defined crystals. The yield was 85 per cent. of the theoretical. Dried in a vacuum over sulphuric acid it melted with decomposition at 102°–103° (Perkin[1] gives 104°). The decomposition-point was found to depend to some extent upon the rapidity of heating. The analysis gave the following results:

0.1582 gram of substance gave 0.3814 gram of carbon dioxide, and 0.0766 gram of water:

	Calculated for $C_6H_5COCH_2COOH$.	Found.
C	65.85	65.80
H	4.91	5.38

Heated to 110° it decomposed into carbon dioxide and an oil, which was insoluble in alkalies, and had the characteristic odor of acetophenone. It gave with phenylhydrazine a crystalline hydrazone, melting at 105° (characteristic of acetophenone).

The ethoxycinnamic acid obtained above was treated like the ester with hydrochloric acid, and the same product, benzoylacetic acid, was obtained. Crystallized from benzene and ligroïn, it decomposed at 102°–103°, and gave the following results on analysis :

0.1456 gram of substance gave 0.351 gram of carbon dioxide, and 0.0698 gram of water.

	Calculated for $C_6H_5COCH_2COOH$.	Found.
C	65.85	65.74
H	4.91	5.33

It has been shown[2] that ethoxyfumaric and ethoxymaleïc esters are converted into oxalacetic acid by saponification with aqueous hydrochloric acid. This is explained by supposing

[1] J. Chem. Soc. (London), **45**, 170.
[2] Michael and Bucher : Ber. d. chem. Ges., **28**, 2512 ; **29**, 1792.

that the hydroxyfumaric or hydroxymaleïc acid is first formed, which then goes over into the saturated acid as follows:

$$\begin{array}{ccc} \text{HC—COOC}_2\text{H}_5 & \text{HC—COOH} & \text{H}_2\text{C—COOH} \\ | & \longrightarrow \quad | & = \quad | \\ \text{H}_5\text{C}_2\text{OC—COOC}_2\text{H}_5 & \text{HOC—COOH} & \text{OC—COOH.} \end{array}$$
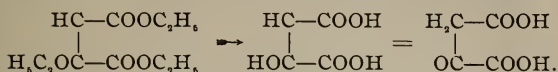
The action of hydrochloric acid upon ethoxycinnamic ester or acid in a similar way may be represented as follows :

$$\text{C}_6\text{H}_5\text{C(OC}_2\text{H}_5)\text{CHCOOC}_2\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{C(OH)CHCOOH} =$$
$$\text{C}_6\text{H}_5\text{COCH}_2\text{COOH.}$$
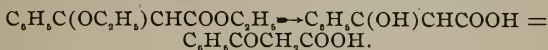
It is therefore β-ethoxycinnamic acid.

β-Ethoxycinnamic acid is a white, crystalline solid, almost insoluble in cold water, soluble in alcohol, sparingly soluble in ether, slightly soluble in cold and easily in hot carbon tetrachloride and benzene, insoluble in cold ligroïn. It crystallizes from solution in carbon tetrachloride, or when a solution of its salt is acidulated, in thin, transparent, truncated prisms, which melt with decomposition at 164°–165°.

The silver salt, made by treating the ammonium salt with silver nitrate, is formed as a white crystalline mass, which under the microscope appears in the form of fine needles. The air-dried salt does not lose weight when heated to 100°. Dried in a vacuum at 100° it gave the following analytical results:

0.2132 gram of substance gave 0.0766 gram of silver.

	Calculated for $\text{C}_6\text{H}_5\text{C(OC}_2\text{H}_5)\text{CHCOOAg.}$	Found.
Ag	36.09	35.94

The calcium salt crystallized from a moderately concentrated solution in white needles (the crystallization is greatly facilitated by boiling the solution), which air-dried gave the following results on analysis :

0.201 gram of salt gave 0.0479 gram of calcium sulphate.

	Calculated for $[\text{C}_6\text{H}_5\text{C(OC}_2\text{H}_5)\text{CHCOO}]_2\text{Ca,8H}_2\text{O.}$	Found.
Ca	7.07	6.98

The water of crystallization was not determined directly as the salt began to decompose before all the water was expelled.

The copper salt is crystalline and slightly soluble in water. The lead and zinc salts are also slightly soluble.

Diethoxyphenylpropionic Ester.

The first portion of the distillate, obtained by treatment of dibromhydrocinnamic ester with sodium ethylate (page 136), owing to the small quantity of substance and slight decomposition on distillation could not be entirely purified by fractionation. It gave the following results on analysis:

0.2038 gram of substance gave 0.5158 gram of carbon dioxide, and 0.1444 gram of water.

	Calculated for $C_6H_5C(OC_2H_5)_2CH_2COOC_2H_5$.	Calculated for $C_6H_5C(OC_2H_5)_2CHCOOC_2H_5$.	Found.
C	67.63	70.80	69.01
H	8.33	7.30	7.87

It was therefore evidently a mixture of the two esters.

A small quantity saponified with a four per cent. solution of caustic potash in ninety per cent. alcohol, by standing in the cold, gave on acidulating with sulphuric acid, benzoylacetic acid, which, crystallized from benzene and ligroïn decomposed at 102°–105° into carbon dioxide and acetophenone.

To show that benzoylacetic acid is not formed by saponification of ethoxycinnamic ester by aqueous potash in the cold, a small portion of this ester was treated with a slight excess of a four per cent. solution of aqueous caustic potash, and allowed to stand with occasional shaking, for two weeks, at ordinary temperature. It finally nearly all went into solution. Acidified with sulphuric acid, ethoxycinnamic acid separated as before ; recrystallized from carbon tetrachloride and dried in a vacuum over sulphuric acid, it melted with decomposition at 163°–164°.

The formation of benzoylacetic acid is explained in the same way as the formation of oxalacetic acid from ethoxyfumaric ester.[1] It has been shown[2] that in alcoholic solution unsymmetrical diethoxysuccinic acid is first formed, which when heated is decomposed to oxalacetic acid, and not, as Nef supposed, saponifying directly to hydroxyfumaric acid. In the above case unsymmetrical β-diethoxyphenylpropionic

[1] Nef : Ann. Chem. (Liebig), **276**, 226.
[2] Michael and Bucher ; Ber. d. chem. Ges., **28**, 2512 ; **29**, 1792.

ester should first be formed, which, being unstable under the conditions of the experiment, would be decomposed to benzoylacetic acid.

The above-mixed esters, saponified with aqueous hydrochloric acid, gave pure benzoylacetic acid.

Pure ethoxycinnamic ester, treated with sodium ethylate (1 mol.) in an equal weight of absolute alcohol, allowed to stand at ordinary temperature five days, and worked up as usual, gave a mixture of the two esters similar to the original mixture, boiling at 130°–135° at a pressure of 2–2.5 mm. (bath 150°) without decomposition, and gave the following results on analysis:

0.1424 gram of substance gave 0.3638 gram of carbon dioxide, and 0.1063 gram of water.

	Calculated for $C_6H_5C(OC_2H_5)_2CH_2COOC_2H_5$.	Calculated for $C_6H_5C(OC_2H_5)CHCOOC_2H_5$.	Found.
C	67.63	70.80	69.59
H	8.33	7.30	8.22

The Action of Sodium Ethylate upon Citradibrompyrotartaric Ester.

The citradibrompyrotartaric ester used in the following experiments was made from citraconic anhydride, by first converting it into the ester, which distilled at the ordinary pressure at 228°–230°. To this ester, dissolved in an equal volume of carbon tetrachloride, the calculated amount of bromine was added slowly in the the direct sunlight, the mixture being cooled by ice-water. It was allowed to stand a short time in the sunlight, then washed with water and sodium carbonate solution, dried over calcium chloride, the carbon tetrachloride distilled off, and the residue fractionated. The final product boiled constant at 160°–161° under a pressure of 20 mm.

To 20 grams of citradibrompyrotartaric ester, dissolved in an equal weight of absolute alcohol, was added gradually from a drop funnel 2.66 grams (theoretical amount) of sodium dissolved in 36 grams of absolute alcohol. The temperature was kept below 20°. Sodium bromide began to separate out immediately. The solution was allowed to stand sixty-six hours, and at the end of that time it was slightly alkaline. It

was then saturated with carbon dioxide, the sodium bromide and carbonate removed by filtration, the alcohol distilled off in a vacuum on the water-bath, water added and the supernatant oil separated. The aqueous solution was extracted with ether and the etherial solution added to the oil. The whole was then shaken out with a solution of sodium carbonate, and dried over calcium chloride. The ether was distilled off on the water-bath, and the product (9 grams) fractionated in a vacuum. All the fractions contained considerable bromine, which a refractionation failed to remove. It was therefore necessary to use more than the theoretical amount of sodium. To determine this another preliminary experiment was made.

To 20 grams of citradibrompyrotartaric ester in an equal weight of absolute alcohol was added, in the same way as before, 2.96 grams of sodium (theory 2.66) dissolved in 40 grams of absolute alcohol. It remained only slightly alkaline, so 0.3 gram more sodium dissolved in alcohol was added, and the solution allowed to stand several days. It remained strongly alkaline. Worked up as before the crude product showed the presence of bromine, but was freed from it by fractionation.

From 168 grams of ester treated in this way with twenty per cent. excess of sodium ethylate, 87 grams of a neutral oil was obtained. There was also extracted by the sodium carbonate solution, and obtained from this by acidifying with sulphuric acid and extracting with ether, 21 grams of an oil having acid properties. This was not further investigated. The neutral oil was purified by repeated fractionation in a vacuum (with beads), and finally two products were obtained, one boiling constantly at 140° under a pressure of 15 mm. (bath 170°), and the other, a somewhat larger portion, at 157° under the same pressure. The former product gave the following analytical results :

I. 0.1712 gram of substance gave 0.3586 gram of carbon dioxide, and 0.1336 gram of water.

II. 0.1714 gram of substance gave 0.3598 gram of carbon dioxide, and 0.1336 gram of water.

	Calculated for Ethoxycitraconic ester.	Found. I.	II.
C	57.38	57.12	57.24
H	7.84	8.68	8.67

The above ester saponified by a four per cent. solution of caustic potash in the cold, the solution, acidified and extracted with ether, gave on distilling off the ether a thick viscous oil, which, allowed to stand in a vacuum over sulphuric acid in the cold for a long time, did not solidify. An analysis gave the following results:

0.1356 gram of substance gave 0.2412 gram of carbon dioxide, and 0.0733 gram of water.

	Calculated for Ethoxycitraconic acid.	Found.
C	48.28	48.50
H	5.75	6.01

The ester treated with concentrated hydrochloric acid did not give oxalpropionic acid as was expected. Boiled with a ten per cent. solution of sulphuric acid it gave carbon dioxide and propionylformic acid, which treated with phenylhydrazine gave the characteristic hydrazone, melting at 148°–149°[1]. On analysis this gave the following results:

0.1248 gram of substance gave 0.2894 gram of carbon dioxide, and 0.073 gram of water.

	Calculated for $C_2H_5C(N_2HC_6H_5)COOH$.	Found.
C	63.54	63.24
H	6.35	6.50

The salts of ethoxycitraconic acid are very soluble in water, except those of lead and silver. The barium salt can be precipitated with alcohol. An analysis of the salt obtained in this way, and purified by repeated precipitation, gave results as follows:

0.1755 gram of air-dried substance lost, at 100°, 0.0103 gram (= 5.86 per cent. H_2O), and gave 0.1328 gram $BaSO_4$ (= 44.51 per cent. Ba).

Calculated for

$$CH_3—C—COO\diagdown\atop H_5C_2O—C—COO\diagup Ba.H_2O$$

Per cent.
$H_2O = 5.98$
$Ba = 44.34$

[1] Wislicenus and Arnold (Ann. Chem. (Liebig), **246**, 333) found the melting-point 144°–145.° Japp and Klingemann (*Ibid*, **247**, 216) found it 152°.

The higher-boiling portion of the original product (157° at 15 mm.) gave the following analytical results:

0.1828 gram of substance gave 0.3772 gram of carbon dioxide, and 0.1453 gram of water.

	Calculated for Diethoxypyrotartaric ester.	Found.
C	56.50	56.33
H	8.71	8.85

Saponified with dilute caustic potash in the cold, acidifying and extracting with ether, the ethereal solution dried over calcium chloride, the ether partially distilled off on the water-bath, and the remainder in a vacuum over sulphuric acid, it gave a thick oil which failed to solidify on standing. Analyzed without further purification it gave the following results:

0.1848 gram of substance gave 0.3336 gram of carbon dioxide, and 0.1200 gram of water.

	Calculated for Diethoxypyrotartaric ester.	Found.
C	49.09	49.23
H	7.27	7.21

The silver salt is a white crystalline compound, nearly insoluble in water. It does not lose weight at 100°. The analysis of the salt, dried at 100°, resulted as follows:

0.109 gram of substance gave 0.0543 gram of silver.

	Calculated for $C_9H_{12}O_8Ag_2$.	Found.
Ag	49.77	49.81

The lead salt is also nearly insoluble in water; all the other salts made were very soluble, and the barium salt can be evaporated to a syrup without crystallization. The ester saponified by repeated treatment with concentrated hydrochloric acid gave the same product as that saponified with caustic potash. The silver salt of the acid obtained in this way, made by treating with silver nitrate in acid solution, filtering off the small quantity of silver chloride, and neutralizing the filtrate with ammonium hydroxide, gave the following analytical results:

0.063 gram of substance gave 0.0312 gram of silver.

	Calculated.	Found.
Ag	49.77	49.52

The ester boiled with a 10 per cent. solution of sulphuric acid did not give propionylformic acid.

The ethoxycitraconic ester obtained above, dissolved in alcohol, treated again with sodium ethylate (1 mol.) and worked up as usual, gave a mixture of ethoxycitraconic ester and diethoxypyrotartaric ester similar to the original mixture, which could be separated by distillation.

The Action of Sodium Ethylate upon α,β-Dibrompropionic Ester.

The dibrompropionic ester used in these experiments was made from allyl alcohol by adding bromine in a solution of carbon bisulphide, in the sunlight, the solution being cooled by a bath of ice-water, the carbon bisulphide was distilled off and the product purified by fractionation in a vacuum, the final product distilling at 102°–104° at a pressure of 13 mm. (bath 140°). This product was oxidized with nitric acid, and the resulting dibromopropionic acid crystallized out by cooling, washed with nitric acid, and crystallized from ligroïn. It melted at 62°–63°. It was converted into the ester in the usual way.

To 5 grams of the ester dissolved in an equal weight of absolute alcohol, 1 gram of sodium (theory 0.88 gram) in 13 grams of absolute alcohol was added, the temperature being kept below 10°. After standing eight days it was worked up as in the preceding cases. The product contained considerable bromine which could not be removed by fractionation.

10 grams of the ester treated in the same way with 2 grams of sodium (theory 1.76 grams) in 25 grams of absolute alcohol was allowed to stand three days, and then boiled two hours on the water-bath. It became nearly neutral; 0.2 gram more sodium dissolved in alcohol was added, and the solution again boiled two hours. It then remained alkaline; the product worked up as before contained a trace of bromine, which was removed by distillation. 40 grams of the ester treated in this way with an excess of 20 per cent. of sodium gave 13 grams of the neutral oil, and 5 grams of an oil having acid properties was obtained from the sodium carbonate solution

by acidifying with sulphuric acid and extracting with ether; the last product was not investigated.

The neutral oil fractionated in a vacuum began to distil at about 65° under a pressure of 9 mm., the temperature rising gradually to 150°. It was evidently a mixture of two or more substances, and owing to the small quantity of the material at our disposal it was impossible to separate the constituents entirely by fractionation. However, after several distillations, a small quantity was obtained boiling from 64°–65° at 9 mm., which on analysis gave the following results:

0.1925 gram of substance gave 0.4057 gram of carbon dioxide, and 0.1533 gram of water.

	Calculated for ethoxyacrylic ester.	Calculated for diethoxypropionic ester.	Found.
C	58.33	56.84	57.47
H	8.33	9.47	8.84

The analysis therefore indicates that it was a mixture of these two compounds.

Conclusion.

A 20 per cent. excess (over 2 molecules) of sodium ethylate in alcoholic solution acts upon α,β-phenyldibrompropionic ester to form mostly β-ethoxycinnamic ester, with a small quantity of unsymmetrical diethoxyphenylpropionic ester. The reaction may take place in the following stages:

I. $C_6H_5CHBrCHBrCOOC_2H_5 - HBr =$
$$C_6H_5CHCBrCOOC_2H_5;$$
II. $C_6H_5CHCBrCOOC_2H_5 + C_2H_5OH =$
$$C_6H_5CH(OC_2H_5)CHBrCOOC_2H_5;$$
III. $C_6H_5CH(OC_2H_5)CHBrCOOC_2H_5 - HBr =$
$$C_6H_5C(OC_2H_5)CHCOOC_2H_5;$$
IV. $C_6H_5C(OC_2H_5)CHCOOC_2H_5 + C_2H_5OH =$
$$C_6H_5C(OC_2H_5)_2CH_2COOC_2H_5.$$
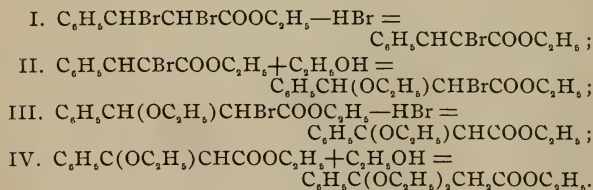
Or the first atom of bromine may be replaced directly as follows:

$C_6H_5CHBrCHBrCOOC_2H_5 + NaOC_2H_5 =$
$$C_6H_5CH(OC_2H_5)_2CHBrCOOC_2H_5,$$
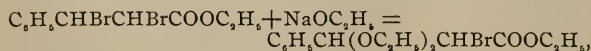
the reaction then taking place as in III and IV.

Unsymmetrical diethoxyphenylpropionic acid is unstable, decomposing and forming benzoylacetic acid.

There was also a small quantity of phenylpropiolic acid formed in this reaction, due probably to the saponification of the ester, and the inability of the salt to take up sodium ethylate by addition.

A twenty per cent. excess (over 2 molecules) of sodium ethylate in alcoholic solution acts upon citradibrompyrotartaric ester to form ethoxycitraconic ester, and, in considerably larger quantity, diethoxypyrotartaric ester. The reaction may be represented as follows :

$$
\begin{array}{l}
CH_3CBrCOOC_2H_5 \\
\quad | \qquad\qquad\qquad + 2NaOC_2H_5 = \\
HCBrCOOC_2H_5
\end{array}
$$

$$
\begin{array}{l}
\qquad CH_3C{-}COOC_2H_5 \\
\qquad\quad | \qquad\qquad\qquad\qquad + 2NaBr + HOC_2H_5 ; \\
\qquad C(OC_2H_5)COOC_2H_5
\end{array}
$$

$$
\begin{array}{l}
CH_3CCOOC_2H_5 \\
\quad | \qquad\qquad\qquad + C_2H_5OH = \\
C(OC_2H_5)COOC_2H_5
\end{array}
$$

$$
\begin{array}{l}
\qquad\qquad\qquad CH_3C(OC_2H_5)COOC_2H_5 \\
\qquad\qquad\qquad\quad | \\
\qquad\qquad\qquad HC(OC_2H_5)COOC_2H_5.
\end{array}
$$
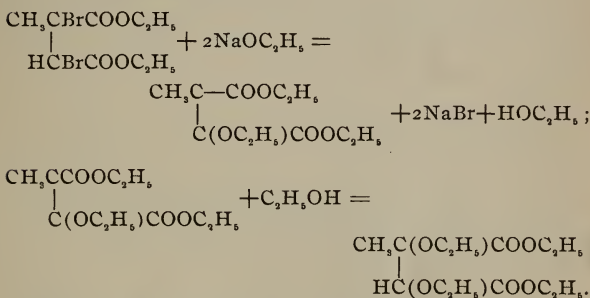
There are two possibilities for the constitution of the last compound. Its behavior towards phenylhydrazine, dilute sulphuric, and hydrochloric acids makes it very probable that it has the symmetrical constitution as given above.

Unsymmetrical diethoxysuccinic acid reacts with phenylhydrazine like oxalacetic acid.[1] Boiled with a 10 per cent. solution of sulphuric acid pyruvic acid is formed.[1] Saponified with hydrochloric acid oxalacetic acid is produced.[2]

The diethoxypyrotartaric acid obtained from the above ester does not react with phenylhydrazine hydrochloride. Boiled with a 10 per cent. solution of sulphuric acid it undergoes decomposition, but does not form propionylformic acid. The ester saponified with hydrochloric acid in the cold gives the same product as that saponified by caustic potash. It is

[1] Michael and Bucher, communicated by the authors.
[2] Michael and Bucher : Ber. d. chem. Ges., **29,** 1792.

therefore very unlikely that it is the unsymmetrical compound.

The experiments with α,β-dibrompropionic ester were so unsatisfactory that no conclusions could be drawn from them.

TUFTS COLLEGE, November, 1897.

Contributions from the Sheffield Laboratory of Yale University.

LVII.—ON SOME BROMINE DERIVATIVES OF 2,3-DIMETHYLBUTANE.

BY H. L. WHEELER.

Theoretically by the action of one molecule of bromine on tetramethylethylene bromide, or, 2,3-dibrom-2,3-dimethylbutane, 2,3,K³-tribrom-2,3-dimethylbutane should result as follows :

$$\begin{array}{c}CH_3 \\ CH_3\end{array}\!\!\!>\!C(Br)-CBr\!<\!\!\!\begin{array}{c}CH_3 \\ CH_3\end{array} \quad\longrightarrow\quad \begin{array}{c}CH_3 \\ CH_2Br\end{array}\!\!\!>\!C(Br)-CBr\!<\!\!\!\begin{array}{c}CH_3 \\ CH_3\end{array}.$$
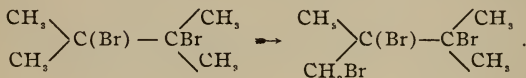
It being immaterial which hydrogen is substituted, only one tribromide would result. Such a compound would be interesting on account of the possibility of converting it into the nitrile of camphoronic acid and this into the acid:

$$\begin{array}{c}CH_3 \\ CH_2CN\end{array}\!\!\!>\!C(CN)-C\!<\!\!\!\begin{array}{c}CH_3 \\ CH_3\end{array} \quad\longrightarrow\quad \begin{array}{c}CH_3 \\ CH_2CO_2H\end{array}\!\!\!>\!C(CO_2H)-C\!<\!\!\!\begin{array}{c}CH_3 \\ CH_3\end{array} CO_2H.$$
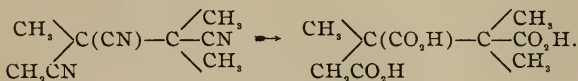
2,3-Dibrom-2,3-dimethylbutane is now readily prepared from pinacone by the methods of Baeyer[1] and Thiele.[2]

However, the action of one molecule of bromine on this compound, which is attacked with exceptional ease, does not give a tribromine compound, but, instead, a tetra derivative results and a corresponding amount of the material remains unaltered.

Linnemann[3] states that when isobutyl bromide is acted on by bromine, no trace of a dibromide is obtained, but a tribromide results exclusively. Linnemann's experiments were conducted at 150°. The author has found that, when this compound is brominated in the presence of iron, the reaction

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[1] Ber. d. chem. Ges., **26**, 2563. [2] *Ibid*, **27**, 455.
[3] Ann. Chem. (Liebig), **162**, 34.

takes place readily on the steam-bath, and a dibromide results, although the yield is poor and the reaction is by no means as smooth as with ethyl and propyl bromides. This dibromide is apparently 1,2-dibrom-2-methylpropane. This result suggested the possibility of obtaining the tribromhexane by the use of iron. 2,3-Dibrom-2,3-dimethylbutane was therefore brominated with iron in carbon tetrachloride, but it was found that a tetrabromide results in this case also.

The product obtained without the use of iron melted constantly at 123° when crystallized from alcohol or ether. When, on the other hand, iron was present, a product melting at 139° was obtained. It was found later, by using carbon tetrachloride as a solvent, that the material melting at 123° was impure and that it contained material melting at 139°–140°, and also a compound melting much higher. It was also found that a mixture of 2,3-dibrom-2,3-dimethylbutane melting at 192°, and the tetrabromide melting at 139° melts at about 123°. It is certain that the same tetrabromide results in both of the above cases. The products had apparently the same solubility and the crystals were identical in appearance.

Bouchardat[1] obtained a tetrabromine derivative from iodhexylene by the action of bromine. This iodhexylene was prepared from pinacone hydrate and hydrogen iodide. He assigns the melting-point 142° to this compound.

It is probable that Bouchardat's product, melting at 142°, and that of the author, melting at 139°, are identical, especially since in both cases the same compound would be expected.

Mariuza[2] prepared a tetrabromhexane from di-isopropenyl, (2,3-dimethyl-1,3-butadiën) and bromine. This, Beilstein[3] states, melts at 131°, and Couturier[4] confirms the preparation of a crystalline tetrabromide from this compound but does not state its melting-point.

By the action of alcoholic potassium hydroxide on 2,3-dibrom-2,3-dimethylbutane the author has obtained an oil, (2,3-dimethyl-1,3-butadiën) which on adding bromine gave a tetrabromide. This, on crystallizing from alcohol and ether, did not melt at 131° but at 139°. From the method of prepa-

[1] Compt. rend., **74**, 810.   [2] Jour. Russ. Chem. Soc., **21**, 435.
[3] The original article is inaccessible to me.   [4] Bull. Soc. Chim. (Paris), [3], **4**, 30.

ration it is concluded that this is identical with Mariuza's compound. It is identical in every respect with the product obtained by brominating 2,3-dibrom-2,3-dimethylbutane. Therefore this compound, the only tetrabromide of 2,3-dimethylbutane known at present, is 2,3,K^2,K^3-tetrabrom-2,3-dimethylbutane and its structure is as follows :

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH_2Br \end{array} CBr—CBr \begin{array}{c} \diagup CH_3 \\ \diagdown CH_2Br. \end{array} \quad (M. P. 139°).$$
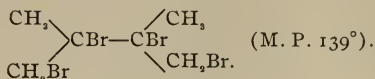
Experimental Part.

2,3-Dibrom,2,3-dimethylbutane, $(CH_3)_2CBr$—$CBr(CH_3)_2$.— This was prepared by the method of Baeyer by saturating a glacial acetic acid solution of pinacone with hydrogen bromide, or by adding pinacone to hydrogen bromide solution saturated at 0° according to Thiele's directions. In both cases the product, on crystallizing from alcohol, melted at 192° or thereabouts. There being some discrepancy in the statements regarding the melting-point of this compound, a bromine determination was made with the result given below. Pawlow[1] states that the compound melts at a temperature higher than 140°, Beilstein credits Eltekow[2] with the statement of 140° as its melting-point, and Kaschirsrky[3] 169°–170°, while Baeyer and Thiele do not mention its melting-point. Couturier[4] states that it melts at 171° in a closed tube, and Kondakow[5] says that on keeping, the melting-point is reduced to 140°. This shows the influence that a slight impurity has on the melting-point of the substance.

A bromine determination in a product prepared by Thiele's method, which melted at about 192°, gave the following :

	Calculated for $C_6H_{12}Br_2$.	Found.
Br	65.6	65.4

2,3-Dibrom-2,3-dimethylbutane, on being mixed with one molecular proportion of bromine, evolves a slow but steady stream of hydrogen bromide. After a number of hours, when the bromine practically disappears, the material washed with

[1] Ann. Chem. (Liebig), **196**, 124.   [2] Jour. Russ. Chem. Soc., **10**, 220.
[3] *Ibid*, **13**, 84.   [4] Ann. Chem. et Phys., [6], **26**, 433.
                   [5] J. prakt. Chem., **54**, 431.

alcohol and crystallized from ether and alcohol—which removes some compound which attacks the eyes—melts then at 123°. A bromine determination gave:

	Calculated for $C_6H_{10}Br_4$.	Found.
Br	79.6	79.1

From ether, on spontaneous evaporation, beautiful minute prisms separated.   These seemed to leave little doubt of the purity of the substance, but, on crystallizing from carbon tetrachloride the melting-point finally rose, and there was obtained a small amount of a substance crystallizing in needles and melting—not sharply—at 162° (Unaltered material?). From the mother-liquor, on standing, needles and granular, stout prisms separated.   The latter melted at 139°–140°.

Owing to the difficulty of purifying the material obtained in the above manner, attention was directed to the bromination in the presence of iron. This proceeds in a smoother manner and more rapidly.

2,3,K^2,K^3-Tetrabrom-2,3-dimethylbutane. — This was obtained when 25.0 grams of 2,3-dibrom-2,3-dimethylbutane (1 molecule), 0.5 gram iron wire and 18.0 grams of bromine (1 molecule + 1.4 grams Br for $FeBr_2$) were mixed in carbon tetrachloride.   The mixture on warming begins to evolve hydrogen bromide, and then further warming is unnecessary. In a short time all the bromine disappears, and this compound separates in granular crystals melting at 139°.   [Analysis I.]

2,3-Dimethyl-1,3-butadiën, $CH_2=C(CH_3)—C(CH_3)=CH_2$. —An attempt was made to prepare 3-brom-2,3-dimethyl-1-butene, $(CH_3)_2CBrC\!<\!^{CH_3}_{CH_2}$, by the action of one molecule of alcoholic potassium hydrate on the dibromide.   The mixture was boiled until it was no longer alkaline. It was then cooled, when unaltered dibromide separated, melting at 192°. The alcohol was distilled off and water was added to the distillate. This gave an oil which was dried over calcium chloride and distilled.   The first and larger fraction boiled from 65° to 80° and contained only a small amount of bromine, the remainder from 80° to 160°. When bromine was added to these fractions, in glacial acetic acid, an immediate precipitate of the

tetrabromide melting at 139° was obtained. It was obtained in larger amount from the lower-boiling fraction. From the fact that the potassium hydroxide was neutralized in the above boiling, and that considerable unaltered material remained, it is concluded that this fraction is chiefly 2,3-dimethyl-1,3-butadiën, and that alcoholic potassium hydrate extracts 2 molecules of hydrogen bromide from 2,3-dibrom-2,3-dimethylbutane. This is confirmed by the fact that a tetra- and not a tribromide is obtained with bromine. A bromine determination in the case of the material melting at 139°, thus obtained, gave the following result : [Analysis II.]

	Calculated for $C_6H_{10}Br_4$.	I.	Found. II.
Br	79.6	79.5	80.0

1,2-Dibrom-2-methylpropane, $(CH_3)_2CBr{-}CH_2Br.-$ When isobutyl bromide is warmed on the steam-bath with iron and bromine, in the proportion to form a dibromide, the reaction is complete in a short time. On washing the product with water and dilute sodium hydrate, an almost colorless oil was obtained. This dried over calcium chloride boiled from about 110° to 214°. On fractioning, a portion was obtained boiling from 146° to 151°, mostly between 148° and 149° *i. e.*, the boiling-point of 1,2-dibrom-2-methylpropane. A bromine determination gave 70.8 per cent. bromine instead of 74.0 per cent. required for a dibromide. This material is therefore mostly 1,2-dibrom-2-methylpropane. From this it will be noticed that bromine in the presence of iron, acts on isobutyl bromide in the same manner as bromine acts on isobutyl iodide. Linnemann[1] states that in the latter case the yield is also poor.

When 2,3-dibrom-2,3-dimethylbutane was boiled with a slight excess of potassium hydrate, in alcoholic solution, an oil was obtained. This was dried over calcium chloride and inadvertently distilled over sodium. On adding bromine to the fraction boiling from 69° to 85°, *i. e.*, the larger fraction, a curious result was obtained. Regenerated 2,3-dibrom-2,3-dimethylbutane separated, melting at about 192°. This low-boiling fraction must, therefore, have contained 2,3-dimethyl-2-butene, which boils at 73°, $(CH_3)_2C{=}C(CH_3)_2$. This suggests that

[1] *Loc. cit.*

2,3-dimethyl-1,3-butadiën, $CH_2=C(CH_3)-C(CH_3)=CH_2$, on partial reduction, does not give 2,3-dimethyl-1-butene, $(CH_3)_x$ $CH-C(CH_3)=CH_2$, but, that a rearrangement takes place giving the above isomeric hydrocarbon. At present the lack of material prevents a further investigation of this subject.

NEW HAVEN, CONN., December, 1897.

PHOSPHATIC CHERT.

BY J. H. KASTLE, J. C. W. FRAZER AND GEO. SULLIVAN.

One of the most characteristic formations in central Kentucky is a deposit of chert which might be called the Lower Hudson chert. This chert marks the upper boundaries of the Trenton limestone and is so persistent and characteristic that it has proven one of the surest guides in the determination of this particular geological horizon. A remarkable feature of the Trenton limestone of Kentucky immediately underlying this deposit of chert is the presence, in the upper portion of it, of thin strata of highly phosphatic limestone, usually of a light brown color. Several years ago Dr. Robt. Peter, chemist of the Kentucky Geological Survey, called attention to these layers of phosphate in our limestone as the probable cause of the remarkable and enduring fertility of the soil of the Blue Grass section of this state.[1] Dr Peter made numerous analyses of the phosphatic limestone from several localities and found them to contain from 1.46 to 31.815 per cent. of phosphoric acid, P_2O_5, the average being about 15.9 per cent. Our attention was again called to these deposits of phosphate in the Trenton by the recent discoveries of workable quantities of phosphate rock in about the same formation near Nashville, Tenn.; and on the May Farm near Lexington, Ky., J. C. Frazer found an outcrop of phosphate rock about $2\frac{1}{2}$ ft. in thickness, and in the soil of the ploughed field immediately overlying this deposit the Lower Hudson chert was found in abundance. In view of the close proximity of the Lower Hudson chert to the phosphatic limestone it occurred to one of us, Mr. Geo. Sullivan, to examine the former for phosphoric acid, with the result that it was invariably found to be present. Since this first observation a great many specimens of this chert have been collected from the following localities

[1] Reports of the Geological Survey of Ky., Chemical Analysis, A., pt.2, p. 184.

in Fayette Co., *viz:* The grounds of the State College of Kentucky, the May Farm, the Frazer Farm, along the line of the Lexington and Eastern R. R., along the line of the Queen and Crescent R. R., from Athens, Ky., and from Fayette Co., near Clarke.

These specimens from these different localities and even from the same locality, have been found to vary quite considerably in color, texture, and hardness. Some of the specimens were found to be hard and flinty, having a conchoidal fracture and in color varying from white to lead-gray or brown; other specimens were white in color, soft and very much like pure clay in appearance; by far the greater number of specimens collected, however, had the appearance of sand-rock and also of being very much weathered. These varieties of the substance varied considerably in color also, passing from almost white through various shades of light brown to dark reddish-brown.

Under the microscope most of the specimens exhibited a honeycomb or cellular structure,—the walls of the cavities being composed for the most part of glassy quartz. The microscopic cavities of the rock were also found to contain a reddish substance closely resembling red clay; probably ferric phosphate. This, however, was usually present only in small amounts. Many of the specimens of chert were found to be fossiliferous, containing fossils characteristic of the Lower Hudson. The chert from the several localities was analyzed with the following results:

Table I, Chert from Lower Hudson.

No. of specimen.	Per cent. P_2O_5.	Per cent. insol. matter.	Description of specimen.
1	0.261	94.43	Like sandstone, color light brown.
2	1.48	88.0	Like sandstone, color light brown.
3	0.217	97.32	Like sandstone but of loose texture. Contains some few fossils.
4	1.64	86.63	About the color of ferruginous clay; matrix of silica easily seen by un-aided eye.
5	0.179	96.60	Like sandstone, color light buff, compact.
6	1.054	92.34	Fossiliferous, color light buff, streaked with dark brown; compact.

No. of specimen.	Per cent. P_2O_5.	Per cent. insol. matter.	Description of specimen.
7	1.05	88.24	Large specimen, about 100 lbs. in weight, dark brown portion.
8	0.57	96.22	From same specimen as No. 7, light portion.
9	0.526	96.4	From same specimen as 7 and 8. The light silicious-looking portion.
10	1.39	88.01	Dark in color, porous, from College grounds.
11	0.965	89.87	Color brown, porous.
12	1.39	76.15	Light-colored silicious specimen.
13	2.8		
14	3.		
15	3.		
16	3.5	....	Porous, dark ; specimens from College grounds.
17	2.		
18	2.1		
19	0.6	....	Hard flinty chert ; small pieces.
20	0.8	....	Clayey chert.
21	2.	....	Very hard white chert.
22	1.42	....	Hard, flinty chert.
23	3.5	....	Very porous and greatly weathered, filled with cavities, spongy in appearance. Color dark-brown.
24	2.	....	Porous, ferruginous, yellowish brown.
25	2.3	....	Mottled dark-brown and white.
26	2.1	....	Light-colored, porous variety.
27	2.5	....	Hard, white and flinty.
28	1.4	....	Dark brownish-gray, porous.
29	2.6	....	Brown and porous.
30	2.8	....	Brown and very porous.
31	2.8	....	Large, light-brown chert, shaped like a bone.
32	2.5	....	Very hard chert, darker in center, found in nodular-shaped masses.
33	1.75	....	Very thick, hard, massive block of chert.
34	0.2	....	White variety, containing shells of gastropoda.
35	0.5	....	Very hard massive chert, light-colored.
36	1.5		
37	1.3	....	Light reddish brown in color.
38	2.5		
39	1.5		

These results certainly show that phosphoric acid while small in amount is a persistent and characteristic constituent of the chert of the Lower Hudson formation, varying from 0.179 to 3.5 per cent. of P_2O_5.   The average of these analyses is 1.684 per cent. of P_2O_5.   As the result of numerous analyses, Dr. Robt. Peter found the average amount of phosphoric acid in the Trenton limestone of Kentucky other than the thin phosphate strata already mentioned to be 0.414 per cent. of P_2O_5,[1] and in 32 of the soils overlying the Trenton limestone this same chemist found an average of 0.328 per cent. of P_2O_5,[2] and in a few remarkably fertile soils of this locality still larger amounts of phosphoric acid, ranging from 0.492 to 0.53 per cent. and to 0.604 per cent. have been observed.   It would thus seem that the Lower Hudson chert contains about four or five times as much phosphoric acid as either the soil or limestone rock of these localities, but a considerably smaller amount than the phosphate rock proper of the upper Trenton. Chert from other localities, *viz.*, from the birdseye (or High-bridge) limestone in Kentucky and from the Permian in Russia, has been examined and found to contain phosphates.

Table II, from Birdseye Limestone.[3]

No. of specimen.	Per cent. P_2O_5.	Description of specimen.
1	3.	White, fossiliferous chert, darker in color on surface.
2	0.75	Very hard compact chert with layer of brown, porous, middle portion.
3	0.5	Very hard, white, massive chert.
4	0.25	Hard, light-brown chert with dark porous surface.
5	0.3	Very hard chert, containing layer of dark spongy substance.

The origin and geological history of chert is still obscure ; and whether this phosphate is original to it or of secondary origin is still an open question.   Certain facts would seem to

[1] Reports of the Geological Survey of Kentucky, Chemical Analyses, pt. 2, Table I, p. 129.

[2] Reports of the Geological Survey of Kentucky, Chemical Analyses, pt. 2, Table B, p. 113.

[3] The specimen of Russian chert was from the Permian, and was furnished by Prof. Miller. It was in the form of a nodule, interior flinty, and contained only traces of phosphoric acid.

point to one conclusion and some to another. The following facts, however, have certainly a bearing upon this problem: First, two specimens of this chert have been found in direct association with the limestone of this formation, that is, as parts of the same rock fragment. In one of these the limestone formed the central portion of the specimen with the chert on the outside. The specimen had a fresh appearance and neither the limestone nor the chert seemed to have been weathered in the least. The chert in this specimen was found to contain 1.36 per cent. of P_2O_5 and 84.92 per cent. insoluble silica or silicates, whereas the limestone center contained only 0.767 per cent. of P_2O_5 and 42.78 per cent. insoluble residue and 56 per cent. carbonate of lime. The results obtained in the case of this specimen would seem to point to the conclusion that the phosphate is an original constituent of the chert; secondly, that the chert had been formed at the same time and by essentially the same process as the limestone; and, thirdly, that there was a gradual passage from limestone to chert: the large amount of insoluble residue in the limestone of this specimen would certainly seem to justify this last conclusion. A second specimen of this chert in intimate association with the limestone, and forming part of the same specimen, was found by A. M. Miller, Professor of Geology in the State College of Kentucky, in a quarry a few miles from Lexington. This specimen consisted of a light gray chert and a lower layer of ordinary limestone and gave the following results on analysis:

	P_2O_5. Per cent.	Insoluble silicates. Per cent.
Cherty portion,	0.34	90.32
Limestone,	0.31	4.06

While this particular specimen shows only a small amount of phosphate it would seem to indicate that it is as characteristic and original with the chert as with the limestone. Further, there is a tradition among certain of the farmers of this locality that those fields in which the chert is found most abundantly are by far the most fertile. This chert may be only the sign and not the cause of this fertility, however, for as has already been observed the phosphate rock of

the Trenton is usually found in intimate association with this chert and hence the increased fertility of these soils may in reality have resulted from the weathering of the phosphate rock.   On the other hand, it should be mentioned in this connection that those cherts which have the appearance of having been most weathered have been found almost invariably to contain the largest amounts of phosphates.   Further, it has been observed that specimens having the darkest color and containing the largest quantities of iron contain also the largest quantities of phosphoric acid.   It is rather difficult to account for this difference in the amount of phosphate in the weathered and unweathered varieties of chert.   It has been suggested to us that it has filtered into the chert from the soil, and hence that the phosphate is of secondary origin.   This of course may be true, but in the light of our present knowledge it is rather difficult to see anything in the nature of the chert that would cause this concentration of the phosphate.   In view of its intimate association with the great deposits of limestone, it would seem more probable that the pores of this chert had once been filled with calcium carbonate containing phosphates, the latter possibly in the form of fossil remains : and that the former having been weathered out by exposure have left the phosphate in relatively larger amount than that contained in the unweathered chert.   Another interesting occurrence of phosphoric acid in this locality which has been discovered in connection with the investigation of the Lower Hudson chert, is a chert breccia which has been found in considerable quantities in the beds of several of our smaller streams.   It was first found in several ploughed fields underlying the Lower Hudson chert.   This chert breccia is dark brown in color, and is composed of fragments of hard, flinty chert, some worn and rounded and others sharp and angular and cemented together by a dark brown material (probably impure phosphate of iron) containing small acicular crystals of manganese dioxide.   Pieces of this substance have been found varying in size from one to two inches in diameter to masses a foot or two across and weighing from one to two hundred pounds.

Specimens, 36, 37, 38, and 39 in Table I. were found along the banks of one of the small streams, in the bed of which oc-

curred large quantities of chert breccia. These pieces of chert had evidently been weathered out of the breccia by the running water. The dark brown cementing material, which often composes quite a large proportion of the entire specimen, is rich in phosphate. The three specimens analyzed gave the following numbers :

	Insoluble silicates. Per cent.	P_2O_5. Per cent.
I.	46.66	4.38
II.	46.58	4.47
III.	44.62	4.5
IV.	....	3.0

We have recently heard of a locality in which the Lower Hudson chert probably occurs in place ; and if this should prove to be the case further studies of this rock will be undertaken. Still other geological formations in this state contain extensive deposits of chert, and these also will be examined for phosphate. The occurrence of phosphates in a silicious material such as chert, is rare and interesting, and may eventually throw light on the origin of this peculiar geological formation.

STATE COLLEGE OF KENTUCKY, LEXINGTON,
December, 1897.

ON THE EFFECT OF LIGHT ON THE COMBINATION OF HYDROGEN AND BROMINE AT HIGH TEMPERATURES.

BY J. H. KASTLE AND W. A. BEATTY.

The combination of hydrogen and chloride to form hydrochloric acid has been, and is still, the subject of a great deal of investigation. The effect of light, especially on this combination, has been very thoroughly studied by Draper, Bunsen and Roscoe, and others. In this connection it has been observed by Amato that a mixture of hydrogen and chlorine, if cooled to −12° C., could be exposed to direct sunlight for hours without combination taking place. Such being the case it occurred to one of us (Kastle) that sunlight ought to cause the combination of hydrogen and bromine, or at least accelerate the change of these elements into hydrobromic

acid, if the temperature be raised sufficiently to enable them to combine at all. So far as could be discovered, no studies of this kind had ever been undertaken. It is stated, however, that hydrogen and bromine do not combine at ordinary temperatures even in the sunlight. In order, therefore, to determine the effect of light on this reaction, a number of glass bulbs were made out of a long piece of glass tubing, in such a way as to leave one bulb connected with another in series by means of a short glass tube of small bore. Hydrogen was then passed through the series of bulbs, and, after they had been filled with the gas, the hydrogen was allowed to bubble through a small quantity of bromine, which had been purified by distillation over sodium bromide, and thus saturated with bromine, it was passed through the bulbs. In this way the bulbs were filled with hydrogen more or less saturated with bromine vapor. The most remote necks of the end bulbs of the series were then sealed off in the flame of the blow pipe; and a series of bulbs thus obtained each of which contained very nearly, if not exactly, the same quantities of hydrogen and bromine. Each bulb was then sealed off in such a way as not to allow any of the gases to escape. The exact amount of hydrogen and bromine, in the bulbs, was not determined; it is known, however, that hydrogen was always present in excess. The hydrogen used in the experiments of series Nos. I. and II., was only purified by passing the gas through potassium permanganate and water; whereas the hydrogen employed in the experiments of series No. III. was very carefully purified by using a little copper sulphate in the sulphuric acid employed in making the gas, and by passing the gas through a solution of copper sulphate, then through one containing potassium permanganate, then through water and a solution of silver nitrate, and finally through pure water. Further, the hydrogen employed in all of the experiments herein described was not dried but used moist. Judging from certain preliminary experiments, it was thought best to work at temperatures in the neighborhood of 200° C.; and *o*-toluidine boiling at 196° C. was selected as a suitable medium in which to heat the bulbs, the manner

of conducting the experiments being about as follows:

The bulbs containing the mixture of hydrogen and bromine were placed in large, thin-walled glass tubes, containing about 50 cc. of *o*-toluidine, and so arranged as to be mainly in the vapor of the boiling toluidine and not in the liquid itself. The large glass tubes were closed with corks bearing a long piece of glass tubing, to serve as a reflux condenser. Some of the bulbs, thus arranged, were heated in the dark, and some in the sunlight. Only bulbs of the same series, of course, were compared as to the effect of light, and the amount of change was measured by the alteration in the color of the bromine.

The following are the results of three series of experiments:

Series No. 1. Temperature 196°.

No. of experiment.	Time.	Condition.	Amount of change.
1	1 hour.	Sunlight.	Change nearly complete, only slight color of bromine remaining.
2	2 hours.	Dark.	Very slight, if any difference in color of bromine. Very little change.
3	$\frac{1}{2}$ hour.	Sunlight.	Color intermediate between 1 and 2. About $\frac{1}{2}$ bromine combined.

Series No. II. Temperature 196°.

No. of experiment.	Time.	Condition.	Amount of change.
1	95 minutes.	Sunlight.	Nearly complete.
2	5 hours.	Diff'd light.	Color intermediate between 1 and 3, this series. About half the bromine combined.
3	3 hours.	Dark.	Color about as deep as in unexposed bulbs. Very little, if any, change.

Series No. III.   Temperature 196°.

No. of experiment.	Time.	Condition.	Amount of change.
1	15 minutes.	Sunlight.[1]	Over 50 per cent. of bromine combined.
2 Same bulb as used in (1)	30 minutes.	Sunlight.	Almost complete — only traces of bromine left.
3	1 hour.	Dark.	No change observable.
4 Same bulb as used in (3)	15 minutes.	Sunlight.	About 50 per cent. change.
5 Same bulb as used in (3) and (4)	15 minutes.	Sunlight.	Intermediate in color between (4) and (6).
6[2] Same bulb as used in (3), (4), and (5)	15 minutes.	Sunlight.	Change nearly complete; only traces of bromine remaining.

These results certainly go to prove that light causes the combination of hydrogen and bromine, at 196° C., the amount of change being proportional to the time of exposure to light. In the dark, at 196° C., the combination of these two gases is exceedingly slow, whereas, in the sunlight, the change is fairly rapid at this temperature. Further, certain results which have been obtained would seem to indicate that light causes the combination of these elements even at 100° C.; although further experiments will be necessary in order to fully establish this point.

[1] The bulbs used in the experiments of Series No. III were the only ones exposed to strong sunlight. During the time of the experiments of Series I. and II., the sky was frequently overcast by thin, white clouds, so that the exposures to the direct sunlight were frequently interrupted.

[2] The bulb used in experiments 3, 4, 5, and 6, was opened and tested for hydrobromic acid. On opening the bulb, dense, white fumes appeared. A little water was run into the bulb and the solution thus obtained gave the well-known reactions of hydrochloric acid.

Further, the results herein described serve to strengthen the analogy existing between chlorine and bromine; and the difference in the temperatures necessary to enable the light to cause the combination of these elements with hydrogen is simply another rough measure of their relative affinity.

A more extended investigation of this subject will be undertaken, and exact measurements made of the rate of this change, at different temperatures, in the light and in the dark. The influence of light on the combination of hydrogen and iodine, at high temperatures, will also be studied.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Dec., 1897.

CHRISTIAN WILHELM BLOMSTRAND.

The Professor of Chemistry and Mineralogy in the University of Lund, Sweden, Christian Wilhelm Blomstrand, died on the 5th of November in his seventy-first year. He began and completed his studies in the University with which he was connected at the time of his death. Three years after he was awarded the degree of Doctor of Philosophy he became assistant to the Professor of Chemistry, and in 1854 he was made instructor. Later he became Professor of Chemistry and Mineralogy, and, after forty years' service, he resigned in 1895 for the purpose of devoting his time to investigation. His name is well known in connection with a large number of investigations in different fields of chemistry, and on account of the originality of the views put forward by him in his book entitled '' Chemie der Jetztzeit vom Standpunkte der elektrochemischen Auffassung aus Berzelius' Lehre entwickelt.'' He did a good deal of work on the rarer metals, as, for example, molybdenum, tungsten, tantalum and niobium, and on many of the complex and rare minerals found in Norway and Sweden, as, for example, monazite, xenotim, ilmenite, tantalite, niobite, etc. One mineral of this group is called Blomstrandite in honor of him.

Among the most interesting of his purely chemical articles is that on the oxygen acids of iodine, in which it was clearly shown for the first time that these acids can be most satisfactorily explained by assuming that in them the iodine is poly-

valent, and that the valence reaches a maximum of 7 in periodic acid. It was shown that the complex periodates could be explained by making this assumption in regard to the valence of iodine, and the view, which was then taken by Blomstrand and seemed startling to timid chemists, has become familiar and is probably quite generally accepted.

Blomstrand also interested himself to a large extent in the diazo compounds, and pointed out a number of years ago that the commonly accepted view is not as satisfactory as another, according to which these compounds appear as ammonium derivatives containing a trivalent and a quinquivalent nitrogen atom. One result of the recent heated discussion between Hantzsch and Bamberger has been to make it clear to the rest of the chemical world that Blomstrand's view is altogether the most satisfactory one. In the last number of the Journal für praktische Chemie, there is an article by Blomstrand on this subject in which he takes the part of Bamberger, and expresses his own ideas with considerable emphasis.

In addition to being an active investigator and a prolific writer, Blomstrand was a teacher of unusual power.

I. R.

REVIEWS.

Precis d' Analyse Chimique. Première partie, Analyse Quali-
tative, deuxieme partie, Analyse Quantitative. Par E. Fink.
Georges Carré et C. Naud. Paris. 1896.

This work, which is divided into two parts, a qualitative and quantitative volume, is evidently intended for the use of practical chemists or of persons who have not had a scientific chemical training, so the information given in these books is of such a nature and so arranged as to serve (to a considerable extent) as a guide to one unskilled in chemical manipulation. In the qualitative part, after giving a list of the necessary reagents, and their method of preparation, the metals are taken up in turn, according to their arrangement in groups, and a list of their insoluble compounds given, with the equations expressing the formation of these compounds and some of their characteristics, in most cases, however, only the color. This is followed by a similar method of procedure in the case of the insoluble salts of the acids, both inorganic and organic, and the usual methods for the separations of the groups and

members of the groups. While on the one hand the book is a mere compendium and of little use to a scientific student of chemistry, on the other hand the matter is presented in such a way as probably hopelessly to bewilder the uninitiated. A general idea of the contents of the volume on quantitative chemistry can be gotten from the table of contents, the six chapters being devoted to the following subjects: Description of apparatus used in quantitative analysis ; General operations of quantitative analytical chemistry; Classification and determination of the metals; Separations of the metals; Determination and separation of the acids ; and Elementary organic analysis.

In the chapter devoted to methods for the determination of the metals, the members of the different groups are taken up in order, and several methods are given for each one. These methods are, however, described very briefly, and in many cases no attempt is made to explain the chemical reaction upon which the method is based. There are of course many persons engaged in practical chemical work, who have been trained to do the work in a mechanical way, and the skill and knowledge gained in this way may enable them to use this book with success. J. E. G.

INTRODUCTION TO ELECTRICAL CHEMICAL EXPERIMENTS. By DR. FELIX OETTEL. Translated (with the author's sanction) by EDGAR F. SMITH, Professor of Chemistry in the University of Pennsylvania. Philadelphia : P. Blakiston, Son & Co. 1897. 144 pp.

A brief notice of the German edition of this book appeared in this Journal last year (Vol. XIX, p. 622). To what was there said it need only be added that the translation will be welcomed by English-speaking students. The translator is well known in connection with the subject of electrochemistry, and we may therefore assume that he has done his work well. This subject is being developed so rapidly that the time may be said to have come when it is necessary for all students of chemistry to familiarize themselves with the methods in use in that subject. This book will furnish teachers with directions for a comparatively simple and yet sufficiently full cours of experimental work for their students, and it is desirab that work of this kind should be introduced into our laboratories as soon as possible. I. R.

RECUEIL DE PROCEDES DE DOSAGE. Par G. ARTH, Professeur de Chimie Industrielle a la Faculté des Sciences de Nancy. Carré et Naud : Paris. 1897.

This book, as the author remarks in the introduction, is not a text-book of analytical chemistry, but only a collection of the specially valuable methods used in the industrial estab-

lishments of France and some others which he has culled from different sources. The subject is treated under three main heads: Analysis of fuel; Analysis of rocks; and Analysis of iron, cast iron, and steel. The methods of analysis and determination of the various factors, which are necessary to determine the value of fuels, are given both for solid fuels, as wood, coke, coal, and related substances, and also for gaseous ones, as blast-furnace gases. The section devoted to mineral analysis gives the methods used for the determination of the different constituents in minerals containing iron; while the last part is devoted to methods for the determination of the carbon, in different forms, phosphorus, silicon, and other constituents of cast-iron and steel. The arrangement of the book is systematic, and the subject is treated in a very compact but thorough manner. The methods are especially selected for their rapidity and accuracy, and in some cases, as the author says in the introduction, a rapid method is given, and also another to act as a check on the more rapid one. The book will no doubt prove valuable to any chemist interested in furnace work and the chemical processes taking place there.   J. E. G.

NOTE.

To the Editor : The great success of the Second International Congress of Applied Chemistry leads us to the belief that the next one, which is to be held in Vienna in July, 1898, will also be numerously attended. Nearly 2,000 members were present at the Paris meeting, and it required five large volumes to contain the report of its proceedings.

The undersigned have been appointed a committee in the United States, to promote the interests of the Third International Congress of Applied Chemistry and beg to call the attention of the chemists of this country to that meeting, with the hope that many may be induced to attend. Those who subscribe and receive their membership cards will be entitled to all reductions in rates going to and coming from Vienna, which are arranged for members of the Congress. During the Paris meeting, the French line of steamers reduced its rates 33 per cent. to members of the Congress. It is hoped that an arrangement can be made with some of the steamship lines during the coming summer for a similar reduction, although

the committee has not yet been informed of any arrangement of this kind.

The opportunity of meeting distinguished chemists from all parts of the world should not be lost sight of, and will doubtless be appreciated by the American members. The scientific work of the Congress will be divided into the following sections:

Section 1.—General analytical chemistry and apparatus, Dr. George Vortmann, Wien, IV Schaumburgergasse 16, chairman.

Section 2.—Food, medicinal and pharmaceutical chemistry, Dr. Ernst Ludwig, Wien, XIX Bilrothstrasse 72, chairman.

Section 3.—Agricultural chemistry, Prof. E. Meissl, Wien, II Trummerstrasse 3, chairman.

Section 4.—Chemistry of the sugar industry, Prof. Friedrich Strohmer, Wien, IV/2 Schönburgstrasse 6, chairman.

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CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

CIII.—ON THE CONVERSION OF METHYLPYRO-MUCIC ACID INTO ALDEHYDOPYROMUCIC AND DEHYDROMUCIC ACIDS.[1]

BY H. B. HILL AND H. E. SAWYER.

The structure of methylfurfurol was established with sufficient precision by Maquenne[2] through its preparation from rhamnose, and this structure was afterward confirmed by Hill and Hendrixson[3], who converted the corresponding methylpyromucic acid into the acetacrylic acid of Wolff[4] by oxidation with bromine in aqueous solution. While the dehydromucic acid of Fittig and Heinzelmann,[5] from the method of its formation, must necessarily have an analogous structure, it seemed to us of interest to prove this relation experimentally by preparing the latter acid directly from methylpyromucic acid.

Hill and Jennings[6] had already described the ω-oxymethyl-pyromucic acid, but their experiments, as well as those which we made ourselves, convinced us that there was little hope of converting this acid smoothly into the corresponding dibasic acid by oxidation. Under all the conditions which we tried

the furfuran ring was itself attacked, and no dehydromucic
acid could be discovered among the products of the oxida-
tion.   As the furfuran ring is not readily opened by dry bro-
mine, it seemed probable that we might accomplish our end
by replacing two or three hydrogen atoms of the methyl group
by bromine.   Hill and Jennings had already found that the
ω-brommethylpyromucic acid could be made without much
difficulty by the action of bromine at high temperature, and
we therefore attempted to introduce a second atom of bromine
by the same method taking this acid as our starting-point.
Although we succeeded in making enough of the ω-dibromm-
ethylpyromucic acid to establish its identity by analysis,
and to show that it could be converted into an aldehyde acid
by the action of water, much more than the theoretical quan-
tity of bromine was required, and the yield was so small that
it would have been impossible for us to prepare in this way
the material needed for a study of the aldehyde acid in ques-
tion.   We therefore turned to the chloranhydride of methyl-
pyromucic acid, and found, as we had hoped, that it was so
much more readily attacked by bromine than the free acid
that it was not difficult in one operation to replace two of its
hydrogen atoms by the action of no very large excess of bro-
mine ; in the course of the reaction the chlorine was also re-
placed by bromine so that the ω-dibrompyromucyl bromide
was the product obtained.   Although it was not easy to pre-
pare this body in a pure condition, the crude product was
formed in satisfactory quantity, and when this was heated
with water it yielded the aldehyde acid which could be puri-
fied without difficulty.

The oxidation of the aldehydopyromucic acid to dehydro-
mucic acid proved to be a simple matter.   The statement of
Heinzelmann[1] that argentic dehydromucate is blackened
when boiled with water, made us hesitate to employ argentic
oxide to effect the conversion.   After we had found that
several other oxidizing agents yielded dehydromucic acid in
but small and varying quantities, we discovered that argentic
oxide in alkaline solution brought about an almost quantitative
oxidation.   The dibasic acid thus formed was then easily

shown to be identical with the dehydromucic acid prepared directly from mucic acid.

In the preparation of the methylpyromucic acid which was needed for this investigation we modified slightly the method recommended by Hill and Jennings in that we substituted sodic hydrate for the sodic carbonate which they used ; and, furthermore, we added this at the outset, instead of waiting until the reduction of the argentic oxide was apparently complete. These modifications made the method more convenient in practice, enabled us to increase the quantity of material employed in each operation, and at the same time slightly increased the yield of the acid. For 30 grams of methylfurfurol we found it best to use about 75 grams of well washed argentic oxide and 11 grams of sodic hydrate dissolved in a liter of water. The argentic oxide was suspended in the dilute solution of sodic hydrate contained in a two-liter flask ; after the mixture has been heated to boiling the methyl furfurol was added and the whole boiled under a reverse cooler for about half an hour. From 197 grams of methylfurfurol boiling at 184°–185° (uncorrected) we obtained in this way 212.6 grams of crude methylpyromucic acid, or 94.2 per cent. of the theoretical amount, so that the yield was nearly quantitative.

Methylpyromucyl Chloride, $C_6H_5O_2Cl$.—In the course of our work we prepared the chloranhydride of methylpyromucic acid, a body which has not yet been described. It may be made most conveniently by the action of a slight excess of phosphoric pentachloride upon the fused and powdered acid. The reaction usually sets in at once at ordinary temperature or after warming gently. It may also be made by the action of phosphorus trichloride upon the acid, a fact that is worthy of note since we have been unable to prepare pyromucyl chloride by the same reaction. Methylpyromucyl chloride is a colorless liquid which boils at 93°–94° under a pressure of 18 mm., and at 202° under a pressure of 756 mm. At low temperature it crystallizes in interlacing needles which melt at 28°. On standing a green color is developed. An analysis showed that it contained the proper percentage of chlorine.

0.3276 gram substance gave 0.3264 gram AgCl.

	Calculated for $C_6H_5O_2Cl$.	Found.
Cl	24.54	24.63

ω-*Dibrommethylpyromucic Acid*, $C_6H_4Br_2O_3$.—Hill and Jennings found that bromine at the boiling-point of chloroform attacked methylpyromucic acid mainly in the methyl group and formed the ω-brommethylpyromucic acid. It seemed, therefore, not improbable that further action under the same conditions might yield an acid containing two bromine atoms in the side chain. Since it had been found that the replacement even of the first hydrogen atom of the methyl group could not be brought about smoothly and required at least twice the theoretical quantity of bromine, it seemed advisable to prepare in the first place pure ω-brommethylpyromucic acid and submit this to the further action of bromine. We modified the method of preparation recommended by Hill and Jennings, only in that we allowed the reaction to proceed in direct sunlight, and used a concave mirror to increase the illumination. Under these conditions we found that the reaction proceeded much more rapidly, and that the yield was at the same time increased; we also took great pains to dry the material used and to exclude all moisture during the operation. We found, however, that twice the theoretical quantity of bromine must be used as before in order to obtain the best yield. All our experiments with ω-brommethylpyromucic acid were carried on in direct sunlight with the aid of a concave mirror. The acid was dissolved in several times its weight of chloroform, and bromine, somewhat diluted with chloroform, slowly added to the boiling solution. Substitution was slowly effected, and it was evident that the reaction was tolerably complex since at least six times the theoretical quantity of bromine was required. After the reaction was completed a part of the chloroform was removed by distillation and the brown viscous residue allowed to stand for some time *in vacuo* over lime. The crystals which separated were then drained on a porous plate, washed with cold ligroïn, and finally recrystallized from benzol with the addition of purified boneblack. The product thus obtained proved to have the composition required by a dibrommethylpyromucic acid.

I. 0.2000 gram substance gave 0.1884 gram CO_2, and 0.0307 gram H_2O.

II. 0.1281 gram substance gave 0.1692 gram AgBr.

	Calculated for $C_6H_4Br_2O_3$.	I.	II.
C	25.36	25.69	....
H	1.42	1.72	....
Br	56.31	....	56.22

The ω-dibrommethylpyromucic acid crystallizes in small greenish-white prisms which melt at 153°. It is quite readily soluble in ether, chloroform, or benzol, very sparingly soluble in ligroïn, and almost insoluble in carbonic disulphide. It dissolves readily with decomposition on heating with alcohol or water; in the latter case hydrobromic acid is formed in abundance, and the aqueous solution then contains a body which reduces argentic oxide and reacts with hydroxylamine and phenylhydrazine. This behavior warrants the conclusion that the two bromine atoms are attached to the carbon of the methyl group. The yield of the ω-dibrommethylpyromucic acid which we could obtain in this way was so extremely small that we made no attempt to prepare it in larger quantities, but tried at once to find a more advantageous method for making the corresponding aldehyde acid.

ω-Dibrommethylpyromucyl Bromide, $C_6H_3Br_3O_2$.—It is well known that the haloid anhydrides of the organic acids are much more open to substitution than the acids themselves; it seemed to us probable, therefore, that we might be able to replace two hydrogen atoms of the methyl group in one operation by treating methylpyromucyl chloride with bromine at high temperature. We found on trial that the reaction ran quietly and smoothly, that a comparatively small excess of bromine was required, and that the yield was tolerably satisfactory. A study of the product soon showed, however, that the chlorine had also been replaced by bromine, so that the ω-dibrommethylpyromucyl bromide had been formed. As in the preparation of the ω-dibrommethylpyromucic acid already described we found that exposure to direct sunlight greatly facilitated the reaction. The methylpyromucyl chloride was heated in a small flask, fitted with a reverse cooler and drop-

funnel, placed in a white porcelain dish containing sulphuric acid which was kept at 150°. The apparatus was placed in bright sunlight, and the light further concentrated upon the flask by means of a concave mirror. In practice we found that about 2.5 molecules of bromine were required to obtain the best results. At first the color of the bromine, as it was gradually added, immediately disappeared with the vigorous evolution of hydrobromic acid, but toward the end of the operation the action proceeded more slowly, and occasionally the color of the bromine was persistent before the whole amount had been added. The hydrobromic acid and the excess of bromine were then driven out by a current of dry carbonic dioxide, and the viscous product allowed to stand *in vacuo* over lime. It gradually solidified in part and the oily impurities could then be removed by means of porous earthenware plates. By repeated recrystallization from chloroform or ligroïn the substance may be further purified, but not without considerable loss of material.

I. 0.2242 gram substance gave 0.1730 gram CO_2, and 0.0230 gram H_2O.

II. 0.2345 gram substance gave 0.3810 gram AgBr.

III. 0.2012 gram substance gave 0.3254 gram AgBr.

	Calculated for $C_6H_3Br_3O_2$.	I.	Found. II.	III.
C	20.76	21.05	....	....
H	0.87	1.15	....	....
Br	69.15	....	69.14	68.82

ω-Dibrommethylpyromucyl bromide, when crystallized from chloroform or benzol, forms thin, elongated plates with pointed ends which melt at 102°; from ligroïn it crystallizes in granular aggregations. It dissolves readily in cold chloroform, benzol, or carbonic disulphide, more sparingly in cold ligroïn, but more freely on heating; on warming with alcohol or water it dissolves with decomposition.

Aldehydopyromucic Acid, $C_6H_6O_4$.—This acid can readily be made by the action of water upon the ω-dibrompyromucic bromide which has just been described. The complete purification of the acid bromide is attended with considerable loss of time and material; we have, therefore, found it much more

advantageous to use for the preparation of the acid crude material thoroughly dried upon porous tiles. When heated with water the body melts and gradually goes into solution. In order to facilitate the reaction we found it convenient to pass in at the same time a current of steam, and noticed that the steam carried over a crystalline body rich in bromine, together with a minute amount of an acid, which could be extracted from the filtered distillate with ether. This acid, from the lack of material, we have been unable to study further, but we have identified the crystalline body as tetrabrommethane. It was readily soluble in ether, chloroform, benzol, carbonic disulphide, or ligroïn, melted at 92°–93°, and contained the proper percentage of bromine.

I. 0.1586 gram substance gave 0.3580 gram AgBr.
II. 0.1488 gram substance gave 0.3359 gram AgBr.

	Calculated for CBr_4.	Found. I.	II.
Br	96.38	96.06	96.06

The aqueous solution left in the flask after distillation with steam was filtered, extracted with ether, and the crystalline residue left by the ether on distillation recrystallized from hot water with the addition of purified bone-black. The acid separates from the aqueous solution either in irregular, curved plates, which are anhydrous, or in long, slender needles, which contain one molecule of water; the anhydrous plates appear to be formed on cooling a hot concentrated solution, while the hydrous needles are formed by spontaneous evaporation at ordinary temperatures. The plates, when thoroughly dried by pressure, lose nothing in weight on exposure to the air, or over sulphuric acid.

0.1241 gram substance gave 0.2337 gram CO_2, and 0.0336 gram H_2O.

	Calculated for $C_6H_4O_4$.	Found.
C	51.42	51.38
H	2.88	3.03

The long needles effloresced rapidly when exposed to the air; for analysis they were dried by thorough pressure between folds of filter-paper.

I. 0.1528 gram substance gave 0.2550 gram CO_2, and 0.0500 gram H_2O.

II. 0.6900 gram substance lost over sulphuric acid 0.0759 gram H_2O.

	Calculated for $C_6H_4O_4.H_2O$.	Found. I.	Found. II.
C	45.56	45.52	....
H	3.82	3.66	....
H_2O	11.40	....	11.00

The dehydrated acid gave the following results :

I. 0.1370 gram substance gave 0.2594 gram CO_2, and 0.0367 gram H_2O.

II. 0.1456 gram substance gave 0.2735 gram CO_2, and 0.0389 gram H_2O.

	Calculated for $C_6H_4O_4$.	Found. I.	Found. II.
C	51.42	51.65	51.24
H	2.88	3.00	2.99

Aldehydopyromucic acid dissolves readily in alcohol, or hot water, more sparingly in ether ; it is sparingly soluble in chloroform, and almost insoluble in benzol, ligroïn, or carbonic disulphide. When quickly heated it melts at 201°–202°, but if the temperature is slowly raised it sublimes with partial decomposition, and the residue melts at a higher temperature. On dry distillation it yields a liquid distillate, which gives a brilliant red color to aniline-acetate paper, showing that furfurol is thus formed with the loss of carbonic dioxide. We have succeeded in preparing no salts which invited further study. The barium salt was very soluble in water, and when precipitated from aqueous solution by the addition of alcohol it gave no satisfactory analytical results ; the sparingly soluble silver salt gave no better results.

Phenylhydrazine Aldehydopyromucic Acid, $C_{12}H_{10}N_2O_4$.— When phenylhydrazine acetate is added to aldehydopyromucic acid dissolved in a solution of sodic acetate, the corresponding hydrazone separates in the form of clustered microscopic crystals. It is readily soluble in alcohol, more sparingly soluble in ether, and almost insoluble in benzol, chloroform, or carbonic disulphide ; it dissolves immediately in dilute sodic hydrate, and is then reprecipitated by the addition

of acids. When quickly heated it melts with decomposition at 176°.

0.1375 gram substance gave 14.9 cc. moist nitrogen at 17° and under a pressure of 768 mm.

	Calculated for $C_{12}H_{10}N_2O_3$.	Found.
N	12.20	12.65

Under somewhat different conditions we obtained a product which contained a higher percentage of nitrogen, but we have made no further study of it.

Oxime of Aldehydopyromucic Acid, $C_6H_5NO_4$.—When hydroxylamine hydrochlorate is added to a concentrated solution of sodic aldehydopyromucate, the separation of the oxime at once begins, and the reaction is soon completed. The granular precipitate can readily be purified by recrystallization from boiling water.

I. 0.2020 gram substance gave 0.3432 gram CO_2, and 0.0629 gram H_2O.

II. 0.1500 gram substance gave 12.4 cc. moist nitrogen at 25°.6 and under a pressure of 746 mm.

	Calculated for $C_6H_5NO_4$.	I. Found.	II.
C	46.43	46.34	....
H	3.25	3.48	....
N	9.06	....	8.98

The oxime is readily soluble in alcohol or ether, but is insoluble in benzol or chloroform; it dissolves freely in boiling water, and as the solution cools the greater part separates unchanged. Even when heated with water in a sealed tube to 150° but trifling decomposition ensues; hydrochloric acid, however, decomposes it rapidly on heating, and hydroxylamine is formed. In a capillary tube it is slowly decomposed, but if rapidly heated it melts with decomposition at 224°–226°.

Dehydromucic Acid, $C_6H_4O_5$.—Aldehydopyromucic acid may be converted into dehydromucic acid almost quantitatively by warming a solution of its sodium salt containing an excess of sodic hydrate with freshly precipitated argentic oxide. The filtered solution is concentrated, acidified with hydrochloric acid, and the dehydromucic acid which separates well washed

with cold water. We found that dehydromucic acid could also be formed by the action of several other oxidizing agents in alkaline solution, but the yield was unsatisfactory. In the course of our work we noticed that an alkaline solution of the aldehyde acid is slowly oxidized by exposure to the air. The dehydromucic acid made by the action of argentic oxide appeared to be identical with that prepared from mucic acid by heating it with a mixture of concentrated hydrobromic and hydrochloric acids according to the method of Klinkhardt.[1] It was sparingly soluble in water, still less soluble in alcohol, sublimed in a capillary tube without melting, and gave the reaction with ferric chloride which is described by Klinkhardt as characteristic. When dried over sulphuric acid it gave the following results :

0.1608 gram substance gave 0.2697 gram CO_2, and 0.0407 gram H_2O.

	Calculated for $C_6H_4O_5$.	Found.
C	46.15	45.75
H	2.58	2.83

The identity of the acid was further established by an analysis of the barium salt, which, according to Heinzelmann[2] and Seelig[3] contains $2\frac{1}{2}$ molecules of water. We found that the salt crystallized in slender, colorless needles, which were permanent in the air, but slowly effloresced over sulphuric acid.

0.6730 gram air-dried salt at 200° lost 0.0900 gram H_2O.

	Calculated for $BaC_6H_2O_5.2\frac{1}{2}H_2O$.	Found.
H_2O	13.38	13.37

0.5830 gram salt dried at 200° gave 0.4658 gram $BaSO_4$.

	Calculated for $BaC_6H_2O_5$.	Found.
Ba	47.15	47.03

[1] J. prakt. Chem., (2). **25**, 43.   [2] Ann. Chem. (Liebig), **193**, 189.
[3] Ber. d. chem. Ges., **12**, 1085.

CIV.—ON THE 3,4,5-TRIBROMANILINE AND SOME DERIVATIVES OF UNSYMMETRICAL TRI-BROMBENZOL.[1]

By C. Loring Jackson and F. B. Gallivan.

In the course of an attempt to prepare the vicinal tetra-brombenzol, which unfortunately did not lead to the desired result, we had occasion to make the 3,4,5-tribromaniline, when to our surprise our product melted at 118°–119°, whereas Koerner, who discovered the substance, says of it, "non fondente a 130°, e che, a quanto pare, si scompone per un più forte riscaldamento."[2] As the statement quoted from Koerner contained all that was known of the properties of the substance, except that he says also that it forms salts, we have made a more careful study of this tribromaniline in order to characterize it. Our melting-point not only differed from Koerner's, but also was essentially identical with that of the ordinary tribromaniline $NH_21,Br_32,4,6$—which melts at 118° according to Koerner, at 119°–120° according to Fittig and Buchner. It was necessary, therefore, in the first place to prove that our substance was the tribromaniline $NH_21,Br_33,4,5$, even although from our knowledge of the positions usually taken by bromine atoms on the benzol ring it seemed hardly possible that a body formed by the action of bromine on paranitraniline could have a different constitution. To make the proof absolute we eliminated the amido group from our tribromaniline, when we found that the vicinal tribrombenzol melting at 87° and crystallizing in tables was formed with remarkable ease. It follows, therefore, that Koerner's statement that the tribromaniline (NH_21,Br_3,Br_4,Br_5) does not melt even at 130° is incorrect, and that it melts at 118°–119°. We have added to the description of the compounds of this tribromaniline which follows an account of some other substances obtained in our attempts to make vicinal tetra-brombenzol, and also a few corrections and additions to our

paper "On Some Derivatives of Unsymmetrical Tribrombenzol"[1] published somewhat more than a year ago.

3,4,5-*Tribromaniline*, $C_6H_2Br_3NH_2$.

To prepare this substance[2] paranitraniline was suspended in water, and converted by the addition of bromine into dibromparanitraniline. Then 50 grams of this product were mixed in a flask with hydrobromic acid (boiling at 125°), and sodic nitrite added in excess. After the last portion of the nitrite had been decomposed, a large excess of hydrobromic acid was added, and the contents of the flask allowed to stand over night. The diazo compound formed was then decomposed by heating on the steam-bath, and the tribromnitrobenzol obtained was reduced with tin and hydrochloric acid without any previous purification, when most of the tribromaniline separated in the solid state, although a small amount could be recovered from the hydrochloric acid solution. It was purified by crystallization from alcohol or hot ligroïn.

Properties.—It crystallizes from alcohol and water in slender white needles, rather short and pointed at both ends. Although it crystallizes in needles like the ordinary tribromaniline, it differs from that in habit, as we could not succeed in obtaining very long needles similar to those which are so characteristic of the NH_2 1, Br 2, Br 4, Br 6 isomer. It melts between 118° and 119°, while the highest melting-point given for the isomeric form is that of Fittig and Buchner, 119°–120°. It is soluble in ether, chloroform, benzol, acetone, or alcohol; slightly soluble in cold, soluble in hot ligroïn; essentially insoluble in water. Dilute alcohol or hot ligroïn is the best solvent for it. It forms salts more readily than the $NH_2$1, $Br_3$2,4,6 tribromaniline, and a little less readily than the $NH_2$1,$Br_3$2,4,5-tribromaniline.[3] With bromine it gives pentabromaniline. By the elimination of its amido group it is converted into the vicinal tribrombenzol melting at 87°.

Chloride of Tribromaniline, $NH_2$1,$Br_3$3,4,5.

This salt could be made by boiling the tribromaniline with

[1] This JOURNAL, 18, 238.   [2] Koerner: Gazz. Chim. Ital., 1874, 347, 390.
[3] This JOURNAL, 18, 247.

a large excess of concentrated hydrochloric acid, but was prepared for analysis by the more convenient method of dissolving the tribromaniline in benzol and adding a strong solution of hydrochloric acid[1] when the salt was precipitated.

0.4976 gram of the salt gave, after the base had been removed by ammonic hydrate, 0.1911 gram of argentic chloride.

	Calculated for $C_6H_2Br_3NH_2Cl$.	Found.
Chlorine	9.69	9.50

Properties.—The salt crystallizes unaltered in white needles from hot water to which a few drops of hydrochloric acid have been added ; but if it is boiled with water alone, it undergoes a partial decomposition. The salt is, therefore, much more stable than the chloride of the $NH_2 1, Br_3 2,4,6$-tribromaniline, which is decomposed completely by water. It is slightly soluble in benzol ; insoluble in ligroïn or ether.

Bromide of Tribromaniline, $NH_2 1, Br_3 3,4,5$.

This salt was made by adding a strong aqueous solution of hydrobromic acid to 2 grams of the tribromaniline dissolved in benzol. The white precipitate formed was filtered out, washed with benzol, dried, and analyzed with the following result :

0.3841 gram of the salt gave, after the base had been precipitated with ammonic hydrate, 0.1771 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NH_2Br$.	Found.
Bromine	19.47	19.63

The bromide resembles the chloride in its properties, and, although slightly more unstable, is still much more stable than the bromide of the tribromaniline, $NH_2 1, Br_3 2,4,6$.

Sulphate of Tribromaniline, $NH_2 1, Br_3 3,4,5$.

To prepare this salt 3 grams of the tribromaniline were heated with moderately strong sulphuric acid. The tribromaniline soon dissolved, and on cooling the solution deposited fine large plates of the sulphate, which were purified by re-

[1] In order to obtain the chloride of the $NH_2 1, Br_3 2,4,6$-tribromaniline, gaseous hydrochloric acid must be used.

crystallization from water slightly acidified with sulphuric acid, dried, and analyzed with the following result:

0.4671 gram of the substance, after treatment with ammonic hydrate, gave 0.1417 gram of baric sulphate.

	Calculated for $(C_6H_2Br_3NH_2)_2H_2SO_4$.	Found.
SO_4	12.66	12.49

Properties.—The salt crystallizes from dilute sulphuric acid in broad, white, shining plates, which are soluble in water; but if its aqueous solution is heated, it decomposes partially into the tribromaniline and sulphuric acid. In the presence of a little sulphuric acid, on the other hand, the aqueous solution can be heated without decomposition. The salt is soluble in alcohol, and its solubility is increased by heat; insoluble in benzol, chloroform, or ether.

Tribromphenylurethane, $C_6H_2Br_3NHCOOC_2H_5$, NH_1, $Br_3$3,4,5.

This substance was prepared by boiling a benzol solution of 10 grams of the tribromaniline with eight grams of chlorcarbonic ethyl ester in a flask with a return condenser. After heating for five hours, as no more hydrochloric acid was given off, the mixture was allowed to cool, when crystals appeared, which were filtered out, and crystallized from dilute alcohol until they showed the constant melting-point 169°–170°. The substance was then dried at 100°, and analyzed with the following results:

I. 0.1915 gram of the substance gave 0.2708 gram of argentic bromide by the method of Carius.

II. 0.1771 gram of the substance gave 0.2473 gram of argentic bromide by the method of Carius.

	Calculated for $C_6H_2Br_3NHCOOC_2H_5$.	Found.	
		I.	II.
Bromine	59.70	60.20	59.43

The $NH_2$1,$Br_3$2,4,6-tribromaniline gives no urethane under these conditions.

Properties.—This tribromphenylurethane crystallizes from a mixture of alcohol and water in thin white rhombic plates frequently with the acute angles bevelled by two other planes, making a very obtuse angle with the sides of the original

rhomb. It melts at 169°–170°; and is easily soluble in alcohol, ether, benzol, or chloroform; essentially insoluble in cold ligroin, soluble in hot. Strong hydrochloric acid in the cold has no apparent action on it. Strong nitric acid or strong sulphuric acid dissolves it, and the addition of water to the solution gives a white precipitate.

When the tribromphenylurethane was boiled with aniline under a reverse condenser, a substance was obtained, after removing the excess of aniline with dilute hydrochloric acid, which crystallized from alcohol in very long needles, melted at 235°, and contained no halogen. There was no doubt, therefore, that it was diphenylurea $(C_6H_5NH)_2CO$, and that the aniline had replaced both the ethoxy group of the ester and the tribromphenylimido group by phenylimido radicals.

Tribromacetanilid, $C_6H_2Br_3NHCOCH_3$, NH_1, Br_3, 3, 4, 5.

Eight grams of the perfectly dry tribromaniline were mixed in small portions at a time with a large excess of acetic anhydride, and the dark-colored solution warmed on the steam-bath for a few minutes. The substance was then precipitated by pouring its solution into water, and purified by many recrystallizations from alcohol, after which it was dried at 100°, and analyzed with the following results:

I. 0.1817 gram of the substance gave 0.2756 gram of argentic bromide by the method of Carius.

II. 0.1114 gram of the substance gave 0.1691 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NHCOCH_3$.	Found. I.	II.
Bromine	64.50	64.55	64.63

Properties.—This tribromacetanilid crystallizes from alcohol in white, slightly radiating brushes made up of very small needles, or in globular groups of needles looking like chestnut burs. It melts at 253°–254°. The tribromacetanilid, NH_1, Br_3, 2, 4, 6, melts at 232° according to Remmers. Our acetanilid is soluble in benzol and in hot alcohol, but only slightly soluble in cold alcohol; soluble with difficulty in ether or chloroform; essentially insoluble in ligroin. Sulphuric acid saponifies it only after long boiling. Fuming

nitric acid converts it into the nitro compound described below.

Tribromnitroacetanilid, $C_6HBr_3NO_2NHCOCH_3$, NHi, $Br_33,4,5,NO_22$.

To prepare this substance 20 grams of the dry tribromacetanilid were added, in small portions at a time, to a quantity of nitric acid of specific gravity 1.50. As the reaction is vigorous, the flask must be cooled and shaken continually during the addition of the acetanilid. The solution thus obtained was poured into water, and the yellowish precipitate crystallized from a mixture of acetone and alcohol until it showed the constant melting-point 229°, when it was dried at 100° and analyzed with the following results :

I. 0.1485 gram of the substance gave 0.2009 gram of argentic bromide by the method of Carius.

II. 0.1624 gram of the substance gave 0.2194 gram of argentic bromide.

	Calculated for $C_6HBr_3NO_2NHCOCH_3$.	I.	II.
Bromine	57.55	57.55	57.49

Properties.—This tribromnitracetanilid crystallizes from alcohol and acetone in white, well-formed crystals, belonging either to the hexagonal or orthorhombic system. When less well crystallized it forms long, very slender prisms terminated by a single plane at an oblique angle, or thick clumps of curving needles. It melts at 229°, and is easily soluble in acetone, soluble in alcohol, slightly soluble in benzol or ether, essentially insoluble in ligroïn. Sulphuric acid saponifies it in time, but this effect is produced much more easily by a strong solution of sodic hydrate.

Tribromnitraniline, $C_6HBr_3NO_2NH_2$, NH_2i, $Br_33,4,5,NO_22$.

This substance was obtained by boiling 10 grams of tribromnitracetanilid with a strong solution of sodic hydrate. As the tribromnitracetanilid was saponified, the solution took on a deep reddish-brown color. When the reaction was complete, the solution was acidified with acetic acid, which threw down a brownish precipitate. This was filtered out and re-

crystallized from alcohol and chloroform until it showed the constant melting-point 130°, when it was dried at 100°, and analyzed with the following results :

I. 0.1912 gram of the substance gave 0.2864 gram of argentic bromide by the method of Carius.

II. 0.2006 gram of the substance gave 0.3017 gram of argentic bromide.

III. 0.2624 gram of the substance gave 18.1 cc. of nitrogen at a temperature of 19°.4 and a pressure of 761.2 mm.

	Calculated for $C_6HBr_3NO_2NH_2$.	I.	Found. II.	III.
Bromine	64.00	63.77	64.01	....
Nitrogen	7.47	....	....	7.93

Properties.—This tribromnitraniline crystallizes from alcohol in yellowish orange needles arranged in radiating groups. If the cooling is rapid, little circular masses of needles are formed. It melts at 130°, and is easily soluble in alcohol, ether, benzol, or chloroform ; essentially insoluble in ligroïn or in cold water ; slightly soluble in boiling water.

In the hope of converting the tribromnitraniline just described into a tribromnitrobenzol, from which the vicinal tetrabrombenzol might be obtained, we submitted it to the diazo reaction as follows : 14 grams of the tribromnitraniline were dissolved in boiling alcohol previously acidified with sulphuric acid, and 10 grams of powdered sodic nitrite added in small portions at a time. The mixture was then boiled for thirty minutes and allowed to stand over night at ordinary temperatures. Upon adding water a yellowish precipitate was formed, which, after recrystallization from alcohol, melted at 230°. An analysis indicated that the substance was the phenol $C_6HBr_3NO_2OH$, although the agreement between the percentage of bromine found and that calculated left much to be desired. (Calculated per cent. of bromine, 63.83. Found, 64.54.) Unfortunately, we did not have enough substance for more thorough purification ; but its properties showed plainly that it was a phenol, as it dissolved in a solution of sodic ethylate forming a reddish-brown salt, from which the original substance was recovered by acidification. As, therefore, this line of work evidently would not lead to

the vicinal tetrabrombenzol, we did not think it worth while to undergo the large amount of labor necessary to prepare more of this phenol in order to characterize it more satisfactorily.

Tribromphenylurethane, $C_6H_2Br_3NHCOOC_2H_6, NHI, Br_3 2,4,5.$

This substance was prepared in order to characterize more fully the tribromaniline $NH_21, Br_3 2,4,5$, described in our first paper.[1] 10 grams of the tribromaniline dissolved in benzol were heated with 8 grams of chlorcarbonic ethyl ester in a flask with a return condenser, until no more hydrochloric acid was given off. The product thus obtained was crystallized from alcohol, until it showed the constant melting-point 101°, when it was dried and analyzed with the following result :

0.1432 gram of the substance gave 0.2016 gram of argentic bromide by the method of Carius.

	Calculated for $C_6H_2Br_3NHCOOC_2H_5.$	Found.
Bromine	59.70	59.92

Properties.—This tribromphenylurethane crystallizes from alcohol and water in long, slender, white needles in radiating bunches, forming a thick felted mass. It melts at 101°, and is freely soluble in alcohol, ether, benzol, chloroform, or glacial acetic acid ; insoluble in water. When it is heated with aniline it yields diphenylurea melting at 235°, and the tribromaniline, which was recognized by its peculiar odor. Its behavior, therefore, in this respect, is like that of the tribromphenylurethane $NHI, Br_3 3,4,6$, previously described in this paper.

Tribromnitracetanilid, $C_6HBr_3NO_2, NHCOCH_3, NHI, Br_3 2,4,5.$

This substance was prepared from the corresponding acetanilid described in our previous paper.[2] We have not determined the position of the nitro group, but should suppose it would be ortho to the acetamido group, and therefore 6. 5 grams of the tribromacetanilid were added in small portions at a time to about 40 grams of nitric acid of specific gravity

[1] This JOURNAL, 18, 247.   [2] *Ibid*, 18, 249.

1.50. The mixture was allowed to stand an hour at ordinary temperatures, and then poured into a large volume of cold water ; the precipitate was recrystallized from alcohol until it showed the constant melting-point 228°, when it was dried at 100° and analyzed with the following result :

0.1001 gram of the substance gave 0.1348 gram of argentic bromide by the method of Carius.

	Calculated for $C_6HBr_3NO_2NHCOCH_3$.	Found.
Bromine	57.55	57.33

Properties.—This tribromnitracetanilid crystallizes from hot alcohol in little, branched needles, generally arranged in circular radiating groups, or in sheaves. It was pinkish white, but is probably white when perfectly pure. It melts at 228°, and is freely soluble in ether, benzol, chloroform, carbonic disulphide, or glacial acetic acid. Sulphuric acid, when boiled with it, converts it into the tribromnitraniline described below.

Tribromnitraniline, $C_6HBr_3NO_2NH_2, NH_2 1, Br_3 2, 4, 5$.

Ten grams of the tribromnitracetanilid were heated in a flask with a return condenser, with sulphuric acid diluted to the specific gravity 1.44, until the solid went into solution. The solution after it had cooled, was diluted with water, neutralized with dilute sodic hydrate, and the brownish precipitate purified by recrystallization from alcohol. When it showed the constant melting-point 130°, the substance was dried at 100°, and analyzed with the following result :

0.2341 gram of the substance gave 0.3513 gram of argentic bromide by the method of Carius.

	Calculated for $C_6HBr_3NO_2NH_2$.	Found.
Bromine	64.00	63.87

Properties.—This tribromnitraniline crystallizes in rather thick yellow needles, often united longitudinally, and sometimes very much branched. It melts at 130°, and is very soluble in ether, benzol, chloroform, acetone, ligroïn, or carbonic disulphide ; soluble in alcohol ; soluble with difficulty in hot water.

Behavior of Tribromdinitrobenzol $(Br_3 1,2,4 (NO_2)_2 3,5)$ *with Sodic Ethylate.*

This reaction was described in our previous paper,[1] but, unfortunately, in determining the composition of the principal product, we relied only on a bromine determination. On returning to the subject we realized that this was entirely insufficient to settle the nature of the body, since the ethoxy group has nearly the same molecular weight, 45, as the nitro group, 46, and therefore our bromine determination would serve equally well for a tribromresorcine (the composition which we had assigned to it, percentage of bromine 59.55), or for a tribromnitrophenetol (percentage of bromine 59.40). We accordingly prepared some more of the substance and tested for nitrogen, when to our great mortification we found that it was present, and that the substance therefore is tribromnitrophenetol, and not tribromresorcine. We regret exceedingly that our carelessness should have introduced this mistake into the chemical literature. Its composition was definitely settled by the following analyses :

I. 0.2430 gram of the substance gave 0.3407 gram of argentic bromide by the method of Carius.

II. 0.3797 gram of the substance gave 11.9 cc. of nitrogen at a temperature of 26° and a pressure of 766.5 mm.

	Calculated for $C_6HBr_3NO_2OC_2H_5$.	I.	II.
Bromine	59.40	59.67	....
Nitrogen	3.47	....	3.51

Properties of Tribromnitrophenetol.—These were given in our first paper as the properties of tribromresorcine ; we therefore think it best to repeat them here under the true name. It crystallizes from alcohol in long, white, pearly plates terminated by two planes at an acute angle, which is usually truncated by a basal plane. It melts at 158°. It is nearly insoluble in cold alcohol, soluble in hot ; soluble in chloroform, benzol, or acetone ; slightly soluble in cold ligroïn, more soluble in hot. The best solvent for it is hot alcohol.

In the aqueous filtrate from the tribromnitrophenetol we found the salt of a diatomic phenol melting at 67°, to which, in our

[1] This JOURNAL, 18, 244.

previous paper, we assigned the formula $C_6HBr(NO_2)_2(OH)_2$, on the ground of a bromine determination. In returning to the subject we thought it well to obtain more analytical data in regard to it, and for this purpose we have made and analyzed the barium salt.

Barium Salt of Bromdinitroresorcine(?), $C_6HBr(NO_2)_2O_2Ba$.

The constitution of the phenol has not been proved; but, as according to analogy the two hydroxyls should be in the meta position to each other, we have adopted the name given above provisionally.

The barium salt was prepared as follows: 2 grams of the phenol were mixed with a freshly prepared alcoholic solution of sodic ethylate, and then treated with an aqueous solution of baric chloride. The yellow precipitate thus obtained was filtered as quickly as possible, washed three times with a little cold water, and once with ether, and then dried at 130° and analyzed with the following result:

0.2580 gram of the salt gave 0.1464 gram of baric sulphate.

	Calculated for $C_6HBr(NO_2)_2O_2Ba$.	Found.
Barium	33.09	33.36

This analysis, therefore, confirms our previous view of the composition of the phenol.

Properties.—The barium salt is an orange-yellow powder with no well defined crystalline form. When heated in the flame of a Bunsen lamp it explodes. It is soluble in water, and its solubility is increased by heat; slightly soluble in alcohol; insoluble in ether, chloroform, or ligroïn. Acids set free the phenol $C_6HBr(NO_2)_2(OH)_2$ from it.

CV.—A CONVENIENT GAS GENERATOR, AND DEVICE FOR DISSOLVING SOLIDS.

By Theodore William Richards.

Since the days when Priestley and Cavendish evolved their oxygen and hydrogen from very simple apparatus, many scores of contrivances for accomplishing the same end have burdened the pages of chemical periodicals. Among these

many contrivances, the patient reader may find an apparatus to suit almost any particular exigency ; but most of the suggestions are unsatisfactory in at least one of the following respects. The apparatus suggested is apt to be either excessively complex, inconveniently brief in its time of effective action, or very inconstant as to the pressure of the gas delivered. In avoiding the last two faults, the suggester has usually run into the first, which does not always trouble the inventor as much as it does the user of the invention.

Perhaps the best of the many usual forms of apparatus, when large quantities of gas are desired, is that in which the liquid is allowed to fall drop by drop upon the solid, the saturated liquid being drawn off at the bottom.[1] The chief disadvantages of this apparatus are that a stop-cock regulated for delivering very small amounts of liquid is apt to be clogged by accidental obstruction ; that it is hard to regulate the drops of liquid so as to produce just the desired flow of gas ; and that the outflow of the partly exhausted but usually unsaturated liquid is apt to produce serious changes in the pressure of the gas, even if this outflow is arranged automatically. A simple apparatus which could supply fresh acid when needed and only when needed, and at the same time could carry off the refuse automatically without change of pressure, would evidently be a desirable improvement.

No startlingly new principle is to be expected in a new device to accomplish these ends, and none will be found in the apparatus described below. The idea of using the heavier specific weight of the exhausted solution in order to remove it and give place to the fresh supply, has been used by many experimenters,[2] and indeed Wollny, Sleenbuch, and Reatz have described apparatus similar in principle to the one independently invented to supply a long-felt need in this laboratory. The chief gain of the present apparatus is its great simplicity,

[1] Seidler : Chem. Centrbl., 1884, 98 ; Gawalovski : *Ibid*, 1885, 369 : Breyer : *Ibid*, 1889 (2), 627 ; Ostwald : Ztschr. anal. Chem., 1892, 183 ; Mirus : Chem. Centrbl, 1894, (1), 706 ; N. Teclu, Ztschr. anal. Chem., 1894, 441, etc. Ostwald's apparatus is probably the best of these ; but in it the pressure is very inconstant.

[2] Wollny : Ztschr. anal. Chem., 1885 (Vol. 24), 214 ; Sleenbuch : J. prakt. Chem., 1887 (Vol. 35), 364 ; Burgmeister : Chem. Centrbl., 1890, (1), 626 ; Raikow : *Ibid*, 1891, (1), 522 ; Reatz : Ztschr. anal. Chem., 1892, 415 ; Kalecsinsky : Chem. Centrbl, 1892, (2), 1058 ; Harris : J. Am. Chem. Soc., 17, 809 ; Völler : Chem. Centrbl, 1896, (1), 1153 ; Norton : J. Am. Chem. Soc., 18, 1057 ; Andrews : Chem. Ztg., 1897, 667.

which places it within the reach of every one, even the elementary student.

The accompanying sketches speak for themselves. The vessel containing the solid reagent is suspended half-way in a tall jar containing the liquid, in such a way that the heavy solution produced by the reaction is removed by a long tube reaching quite to the bottom of the jar. The fresh liquid is drawn up through a tube extending several centimeters into the heart of the generator (Figs. 1, 3, 4, and 5), or else supplied through small holes high up in its walls (Fig. 2). This method of supplying new reagent is the chief respect in which the present apparatus differs from previous ones ; by its aid the fresh material is kept almost uncontaminated by the exhausted solution. Thus the circulation continues long unimpaired, and hence the evolution of gas remains remarkably constant. The pressure of the gas thus supplied is determined by the difference between the level of the liquid at its point of delivery and that of the same liquid at its point of contact with the outside air. Since this distance is constant, and the specific gravity of the part of the solution in question does not vary throughout much of the use of the charge, the pressure also remains essentially constant. It is true that this constancy is obtained at the sacrifice of a part of the otherwise available height of the jar, but since tall cylinders are easily obtainable, this is no great objection. Moreover, if one uses the most satisfactory means of purifying and drying the gas—tall vessels filled with beads, which are moistened with a counter-current of purifying liquid,[1]—no great pressure is necessary. The tube containing the regulating stopcock should always be arranged horizontally, in order that it may not be clogged by accumulating liquid.

The degree of saturation of the used solution is of course influenced by the size of the lumps of solid, by the depth of layer of solid through which the liquid must pass, and by the rate of the gas current drawn off. If it has not been very nearly saturated at first, the partly used solution will be drawn through the generator again ; but this time the gas will be evolved at a slightly less pressure, for the specific

[1] Proc. Am. Acad., **32**, 68.

SECTIONAL DIAGRAMS OF GENERATORS AND DISSOLVER.

A = vessel for containing the solid.   B = enlarged view of acid inlet tube.
C = wire for supporting or lifting the lower part of the apparatus.
D = drying apparatus to protect the gas stop-cock from condensed moisture.
E = stop-cock for withdrawing exhausted solution.   F = handle.   G = glass-wool.
By making the tube H flexible, the pressure may be altered at pleasure.
I = inlet holes for fresh solvent.   In Fig. 7 these holes, large in size, may be loosely
    plugged with glass-wool.
Each piece of apparatus is more satisfactory if the solid is supported upon beads.
The arrows indicate the direction of the liquid current.

gravity of the liquid in its delivery tube has somewhat increased. It is surprising how sharply marked is the dividing line between the used and unused solutions in the jar below. Of course it is possible to draw off the saturated liquid at any time, by means of a siphon or tap at the bottom of the jar, replacing it by fresh liquid poured in above, without stopping the evolution of the gas.

Several forms of the generator are given below. That depicted in Fig. 1 has the advantage of ready construction from materials at everyone's command. Since the small rubber stopper is water-sealed, there is no danger of leakage, even with hydrogen. The small tube inside for delivering the liquid may advantageously be supplied with a few fine holes, as is shown in the enlarged detail at the right. The form shown in Fig. 2 may be employed when rubber must be eschewed, since it consists wholly of glass, the two parts being held together by a platinum wire. It is superior to the other in every respect except two : the solutions are not kept quite so sharply distinct, and the charging of the apparatus in the first place is a little more awkward. Neither of these objections is serious, however. It is sometimes advisable to use very dilute solutions of hydrochloric acid in the generator, because very dilute solutions yield a gas which is scarcely at all contaminated with acid. For this requirement, the arrangements shown in Fig. 3, 4, or 5 are well adapted. The third simply replaces the cylinder of the earlier forms by a long- and wide-necked flask, while the last consists of an easily made combination of a small bottle deprived of its bottom, a Wolff bottle, some tubes, and a bulb or funnel. The fourth is an obvious adaptation of the same idea. The fourth and fifth have the advantage of giving almost any pressure desired. In Nos. 3, 4, and 5, acid as dilute as normal may be used with success ; hydrochloric acid of this strength yields a gas containing only about 0.002 milligram of chlorine per liter.

Since dissolved zincic sulphate of about 5.7 times normal strength, and ferrous sulphate of about 3.3 times normal strength, begin to crystallize at 10°, it is well not to use sulphuric acid of higher specific gravity than 1.18 or 1.10, re-

spectively, when one of these two substances is to be a product of the reaction.

It is hoped that the ease of making and filling these simple pieces of apparatus, and the constancy of their operation, may commend them to the use of chemists, and cause them to supplant the clumsy, inconvenient, and inconstant apparatus of Kipp. By using two generators side by side, even the solid reagent may be renewed without interrupting the current of gas; and two of these generators are far easier to make than one of the complexity of Wollny's, the apparatus which comes nearest to accomplishing the same end.

These gas generators are naturally only of service when the residual solution is heavier than the initial solution. For the preparation of hydrochloric acid from salammoniac, where the exhausted solution is lighter than the strong sulphuric acid used, Wollny[1] has devised a suitable, although somewhat expensive, piece of apparatus. The same end may be accomplished by conveying off the exhausted liquid with the help of an inverted siphon, which will raise the lighter liquid from a lower to a higher level without interfering with the evolution of the gas. The viscosity of the solution, and its consequent frothing, so much complicate the manipulation of this siphon that it is not to be recommended for common use, however. Ordinarily a simple cylinder containing the sal ammoniac, immersed in a jar of acid, answers every purpose; because a momentary stoppage of the gas-current at once drives out the refuse, which rises to the top, and thus leaves room for fresh reagent. It is almost needless to add that a Kipp generator is very unsuitable for this purpose.

It is obvious that a device giving a saturated solution opportunity to remove itself by virtue of its increased weight may be used to conduct the rapid and automatic dissolving of crystals; and if the lower part of the receptacle for the solid is plugged with glass wool, the solution may be filtered while it is being made. Two forms of this device are shown in Figs. 5 and 6, the former being more easily made, and therefore more generally acceptable, while the latter is more satisfactory if the crystals contain impurities specifically lighter than

[1] *Loc. cit.*

the solution. To give an example of the working of this lit-
tle instrument, whose underlying principle has undoubtedly
been used by scores of chemists before, the following experi-
ment may be cited : 30 grams of cupric sulphate placed in
the '' dissolver'' required ninety minutes to dissolve in 200 cc.
of water when no glass wool was used, and less than three
hours when the solution was simultaneously filtered. The
same weight of material in the same-sized crystals (averaging
about 2 grams apiece) required fifteen days to dissolve in the
same amount of water, at the same temperatue ($20°$ ±), un-
disturbed in a beaker.

The '' dissolver'' cannot fail to be of value to the qualita-
tive chemist who has many solutions to make, for it saves
him the trouble of powdering his crystals and of filtering the
solution after it is made ; and the gas generator, from its
wide applicability and simplicity, ought to be even more use-
ful.

A REDETERMINATION OF THE ATOMIC WEIGHT OF ZINC.[1]

BY H. N. MORSE AND H. B. ARBUCKLE.

It has been shown by Richards and Rogers[2] that oxide of
zinc derived from the nitrate, even when heated to very high
temperatures, retains notable quantities of free nitrogen and
free oxygen. The discovery of this hitherto unsuspected
source of error in those determinations of the atomic weight of
zinc which are based upon the weight of such oxide, made it
necessary to revise the work of Morse and Burton.[3] The ox-
ide which was obtained in the course of their work was not in
condition to be utilized for the correction of the results ; it
was therefore decided to repeat the entire investigation and to
determine as carefully as possible the amount of the gases re-
tained by each specimen of the oxide. Fortunately, we still
had a limited supply of the metal which had been prepared
for the earlier determinations. This, as stated in the account
of that work, had been prepared from Schuchardt's so-called

[2] Proc. Am. Acad. Arts and Sciences, **28**, 200.   [3] This JOURNAL, **10**, 311.

"absolutely chemically pure metallic zinc" by repeated distillation in a vacuum, and contained no impurities which could be detected by chemical or spectroscopic methods. Had it contained the alkalies or calcium, derived from the glass in which the distillations were made, as seems to be suggested by Richards and Rogers,[1] the fact would hardly have escaped detection when the metal was examined spectroscopically with Professor Rowland's ample facilities for refined work in that field.   Furthermore, it may be stated that all parts of the zinc which had been in contact with the glass were removed with a file, it being assumed that whatever the metal acquired from the glass would remain near the surface of contact between the two.

The method of work, up to the point of determining the imprisoned gases, was an exact repetition of the procedure of Morse and Burton.   Briefly stated, it consisted in converting the metal into nitrate in porcelain crucibles, and the nitrate into oxide by heating—moderately at first, but at last in a muffle furnace to a temperature sufficient to melt cast-steel.

Our arrangement for the liberation and collection of the occluded gases is represented in the accompanying figure. The tube *a* is something more than the normal barometric height in length, and of sufficient internal diameter to allow the crucibles containing the oxide to pass upward as the apparatus is exhausted ; *b* is the reservoir for the dilute sulphuric acid which was used to dissolve the oxide ; and *c*, the eudiometer in which the liberated gases were collected.   The stop-cocks *d* and *e*, together with the adjacent portions of the glass tubes above and below them, were washed with a solution of mercuric chloride and immersed in mercury.   The troughs for the mercury in which the stop-cocks were buried consisted of two parts, one of which fitted the back side of the apparatus at those points, and the other, the front.   The two parts were held together by screws when in position.   The spaces between the two halves of the troughs, and between the glass parts and the wood, were filled with an elastic gum, and the troughs were given supports which were independent of those which held the rest of the apparatus in position.

1 Ztschr. anorg. Chem., **10**, 2.

The eudiometer *c* was so narrow in the upper part that a milli-
meter division on the scale corresponded to only about 0.03
cc. It was, moreover, calibrated with great care. An acid
containing about 28 per cent. of sulphuric acid was found to
dissolve the oxide readily, and this concentration was there-
fore employed throughout the work. The bulb *b*, when half
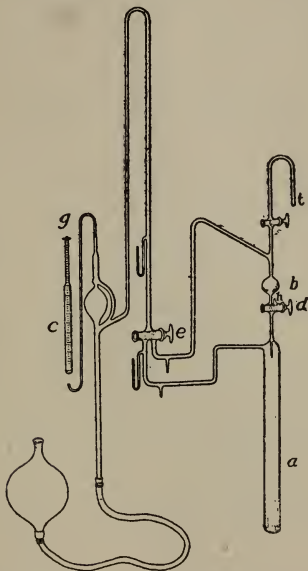
filled, contained enough of the acid for ten or a dozen deter-
minations. The acid was introduced into the bulb and
pumped out until, after standing for several days, no more
gas could be obtained from it.

Having heated the oxide to constant weight in the muffle,
the weighed pair of crucibles[1] were placed in a small crystal-
lizing dish, and inserted in the open end of *a*. The mercury
reservoir was then raised into position by means of screws
and so adjusted that the lower edge of *a* rested evenly and

[1] See This JOURNAL, **10**, 316.

firmly upon a piece of thick rubber packing in the bottom of the reservoir. Finally the mercury was introduced by means of a siphon and the apparatus exhausted, the height of the mercury in *a* being so adjusted in the end that the delivery tube for the acid reached nearly to the bottom of the crucible containing the oxide. As the mercury rose and the difference in pressure between the inner and outer sides of the tube increased, the table on which the reservoir rested was raised from time to time, by means of the adjusting screws in order to prevent *a* from sinking and thus bringing a strain upon the tubes connecting it with the pump.

After exhausting and bringing the crucibles to the proper height with respect to the tube delivering the acid, the apparatus was allowed to stand undisturbed for twelve hours. If no leak developed within that time, the acid was admitted to the oxide. At the close of another period of from twenty to thirty hours, the gas liberated during the solution of the oxide was pumped into the eudiometer.

To determine the oxygen in the mixture of the gases, small quantities of hydrogen were introduced and exploded until no further decrease of volume occurred. Afterwards, electrolytic gas was repeatedly introduced and exploded in order to demonstrate the completeness of the removal of the oxygen. Before making a determination of oxygen, the hydrogen and the electrolytic gas to be used were tested as to their purity by exploding portions of the former with the latter, and portions of the latter by themselves and with air.

We deemed it of importance to inquire into two questions which affect the correctness of the results; the first is, whether the gas remaining after the removal of the oxygen is pure nitrogen; and the second is, whether any portion of the nitrogen remaining in the oxide at high temperatures is possibly in the form of a nitride. To settle the first, the gas residues were exploded with oxygen, to remove the excess of hydrogen, and afterwards examined for us spectroscopically in the physical laboratory of this university by Messrs. Ames and Humphreys. Aside from the substances known to be present—oxygen, water vapor, and nitrogen—nothing was found. The oxygen employed to remove the hydrogen, be-

fore submitting the gas for spectroscopic examination, was obtained by means of the apparatus recently described by Magruder,[1] which, on reversing the poles, gave us a gas containing less than 1 per cent. of hydrogen.

To satisfy ourselves regarding the very improbable presence of a nitride, we reserved the various solutions of the oxide ; and, having determined the amount of sulphuric acid in measured portions of their mixture, we diluted to compensate for the concentration which the acid had suffered in the vacuum, and compared the solution with the original acid by means of the Nessler reaction. It was found that the minute quantity of ammonia originally in the acid had not increased during the solution of the oxide.

In the following table are presented the results of the eight successive determinations which were made after the apparatus and the method had been brought into satisfactory working condition. A larger number could not be made, owing to the limited supply of pure metal at our disposal. The weights given are corrected for air displacement ; and liter volumes of oxygen and nitrogen, under standard conditions, are assumed to weigh here, as at latitude $45°$ and sea level, 1.42923 and 1.25461 grams, respectively. The error resulting from this assumption regarding the weights of the gases is, in our case, wholly insignificant, since a correction of their weights to the latitude and elevation of this place would have changed the result not more than a unit in the third decimal place.

The atomic weight calculated from the weights of the oxide, without correction for the occluded gas, namely 65.33, is higher than that of Morse and Burton, 65.27, by 0.06. Since Richards and Rogers have found that the quantity of the gas retained diminishes with increase of temperature, we conclude that the oxide must have been more highly heated in the latter than in the former series of determinations. We endeavored to maintain as exactly as possible all the conditions under which the former work was done ; but it should be stated that the furnace employed by Morse and Burton was not available for our work, and the one used by us may have been somewhat more efficient, or the quality of the fuel may

[1] This JOURNAL, **19**, 811.

have been better. This difference of 0.06 corresponds to a
difference of about 0.14 cc. of gas per gram of oxide. In
other words, the oxide of Morse and Burton—probably owing
to the lower temperature to which it was heated—retained
approximately 0.14 cc. more gas per gram than ours.

	Weight of zinc.	Weight of oxide.	Uncorrected atomic weight.	Volume of gas. (Standard conditions). cc.	Per cent. oxygen.	Corrected atomic weight. (O = 16)
I.	1.19573	1.48860	65.324	0.468	26.28	65.459
II.	1.03381	1.28707	65.312	0.402	18.14	65.445
III.	1.06519	1.32599	65.349	0.342	18.42	65.459
IV.	1.05802	1.31711	65.338	0.312	18.58	65.440
V.	1.26618	1.57619	65.348	0.521	13.82	65.489
VI.	1.03783	1.29198	65.336	0.408	35.28	65.475
VII.	1.08655	1.35276	65.307	0.412	19.55	65.437
VIII.	1.11364	1.38647	65.307	0.456	18.62	65.447

Mean = 65.328   Mean = 65.457

11.02617 grams of the oxide yielded 3.321 cc. of gas, equiv-
alent on the average to 0.301 cc. per gram of the material.
It is noticeable that, while the proportions of the oxygen and
nitrogen vary within wide limits—of the former from 13.82 to
35.28 per cent., and of the latter from 64.32 to 68.18 per cent.—
the volumes of the two, taken together, are much more nearly
constant. This will appear from the following table, which
gives the volume of gas, per gram of oxide, for the individual
determinations:

	Cc.
I.	0.314
II.	0.312
III.	0.258
IV.	0.237
V.	0.329
VI.	0.315
VII.	0.305
VIII.	0.329

The conclusion to be drawn from these relations is that
reached by Richards and Rogers; namely, that the phenome-
non of gas occlusion is here due to physical causes solely.

There is, however, one inference drawn from the results of
Richards and Rogers for which we find no confirmatory evi-

dence in our data. It is, that the imprisoned oxygen escapes more readily than the nitrogen. In other words, that the proportion of oxygen diminishes with increasing temperature. If we grant that the total volume of occluded gas decreases with rising temperature, which cannot be disputed, also that the oxygen escapes more easily than the nitrogen, we arrive at conclusions which are not in accord with our results. In numbers III. and IV., for instance, the volumes of gas, per unit weight of the oxide, were the smallest—0.258 cc. and 0.237 cc. per gram of oxide, against an average of 0.301 cc.—indicating that the material in these cases had been heated to a higher temperature than in the others. We should, therefore, expect to find in them the smallest percentages of oxygen, but we do not. By the same course of reasoning we should conclude that in numbers V. and VIII., in which the largest volumes of gas were found, we ought also to find the largest percentages of oxygen; while, in reality, the proportion of that gas was, in VIII., not noticeably greater than in III. and IV., and in V. it was the least found in any of the determinations. Again, in numbers I. and VI. we should expect to find only a little more than an average proportion of oxygen, whereas they yielded much higher percentages than were found in any of the other cases. We must therefore conclude that the evidence at our command is altogether against the proposition, that the ratio of the retained gaseous constituents depends upon the temperature to which the oxide is heated. Indeed, if the retention is due to physical causes—to obstruction—it is difficult to understand why the oxygen should escape any more readily than the nitrogen.

As regards the final corrected result, 65.457, it is practically identical with the number 65.458, which is the value obtained from the results of Morse and Burton, when corrected according to the quantity of gas which Richards and Rogers[1] found to be retained by the oxide. It is also very near the number 65.459, which was obtained by Richards and Rogers[2] by the bromine method. It differs, however, from the result—65.404—of the later and more rigidly exacting determinations of Richards himself[3] by 0.053.

[1] Ztschr. anorg. Chem., **10,** 2.   [2] *Ibid.* **10,** 12.   [3] *Ibid.* **10,** 24.

It is to be regretted that the gas volumes to be dealt with in our work were so small, since a moderate error in measurement must produce a considerable effect upon the correction we were endeavoring to make. This difficulty was, of course, foreseen; and we tried to overcome it, as far as possible, by making the eudiometer very narrow, by repeated and painstaking calibrations, and by exercising care in the determination of temperatures and pressures. Under the circumstances we judge that the necessary errors connected with the gas analytical part of our work cannot have exceeded one per cent. of the correction which raised the apparent atomic weight from 65.33 to 65.46. But if these errors were cumulative throughout, instead of compensatory as they were more likely to be, the maximum effect upon the final result would be only a unit in the third decimal place.

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DIRECT NITRATION OF THE PARAFFINS.

By R. A. Worstall.

I.[1]

The literature relating to the action of nitric acid upon aliphatic hydrocarbons is very meagre. In general, the text-books state that these hydrocarbons are either not attacked by nitric acid, hot or cold, or, if attacked, are completely oxidized to carbon dioxide and water.

Those who have been engaged in the study of petroleums, notably Pelouze and Cahours, Schorlemmer, Beilstein and Kurbatow, and Mabery, have noticed that nitric acid acts upon petroleum distillates. But that they regarded this action as taking place between the acid and hydrocarbons other than the paraffins, is shown not only by their published statements to that effect, but also by the fact that boiling these distillates with nitric acid has been recommended and used by each as an efficient means of removing these (supposed) foreign hydrocarbons, and thus of purifying the paraffins.

In general, it seems to have been assumed that the nitric acid acted upon naphthenes contained in the petroleum, but

[1] Preliminary report.

did not attack the paraffins. A striking example of this fact is found in the work of Beilstein and Kurbatow.[1] By boiling a 95°–100° *crude* fraction of American petroleum with four parts of nitric acid (specific gravity 1.38) until the acid was exhausted, they obtained a compound distilling at 195°–200°, and giving figures upon analysis fairly representative of nitroheptane. Apparently never suspecting its formation from heptane, they at once concluded that this American petroleum must contain *naphthenes*, and that this nitroheptane(?) was formed from one of the latter hydrocarbons. As a matter of fact, however, Mabery[2] has shown that American petroleums, in general, contain only very minute quantities of naphthenes. Furthermore, Beilstein and Kurbatow state that the pure heptane obtained by distillation of this fraction after the treatment with nitric acid was scarcely at all attacked by fresh acid. In view of results now obtained, this point may be questioned.

A few investigators have noticed that oxidation results when paraffin hydrocarbons are boiled with nitric acid. Schorlemmer,[3] by the action of nitric acid of specific gravity 1.4 upon hexane, octane, and diamyl, obtained in each case carbonic and succinic acids along with other products which he did not identify, but which he thought to be nitrogen compounds. Beilstein and Kurbatow[4] observed the formation of acetic and succinic acids by the action of concentrated nitric acid upon a 95°–100° distillate of Caucasian petroleum.

Apparently the only work which has ever been done upon the direct nitration of the paraffins is that by Konowalow.[5] By heating normal hexane in sealed tubes to 130° with nitric acid of specific gravity 1.075, he obtained a yield of 30 per cent. of *secondary* nitrohexane. Similarly, from normal octane he obtained a *secondary* nitrooctane. Later,[6] by similar treatment of diisobutyl and diisoamyl he obtained from each the *secondary* and *tertiary* mononitro-compounds, and by acting upon the latter with more nitric acid, the *tertiary* dinitro-hydrocarbons were found. But *in no case* did he observe the formation of a *primary* nitro-hydrocarbon.

[1] Ber. d. chem. Ges., **13**, 2029. [2] This JOURNAL, **18**, 49.
[3] Ann. Chem. (Liebig), **147**, 214. [4] Ber. d. chem. Ges., **13**, 1820.
[5] Compt. rend., **114**, 26. [6] Ber. d. chem. Ges., **28**, 1852.

In a former paper[1] I have noted that heptane and octane are rather readily acted upon by nitric acid, and the preliminary results of an investigation of these reactions which is now in progress are here presented.

Preliminary Experiments.

As the method of boiling with nitric acid, or with mixed nitric and sulphuric acids, has long been employed as a means of purifying petroleum distillates, it seemed to me desirable to obtain some data relative to the action of the acid—especially to ascertain *the limit*, if any, to the reaction.

For a preliminary experiment, a quantity of so-called "sixty-three degree naphtha" was employed. This naphtha was thoroughly treated with an excess of fuming sulphuric acid, washed with caustic soda, and dried. Its specific gravity was then 0.7347 at 20°. It all distilled between 90° and 155° and appeared to consist chiefly of normal heptane and normal octane, with some nonane.

For the study of these reactions the following method has been employed in every case : A weighed quantity of the hydrocarbon is gently boiled with definite quantities of nitric acid, or of mixed acids, in a flask provided with a return condenser (and asbestos stopper) until red fumes of nitric tetroxide cease to be evolved, showing the nitric acid to be exhausted. The two layers are then, after cooling, separated mechanically, fresh acid added to the residual oil, and the treatment continued as long as is desired.

225 grams of the naphtha above described were treated in this way with a mixture of equal weights sulphuric and nitric acids with the following results :

Mixed acids. Grams.	Time. Hours.	Specific gravity of residue at 20°.
150	2	. . . . .
150	2	0.7710
250	2	0.8150
250	4	0.8605
300	2	0.9210

That is, after *twelve hours' treatment*, and the use of about twice the calculated quantity of nitric acid, the naphtha, spe-

[1] This JOURNAL, **19,** 836.

cific gravity 0.7347 at 20°, yielded 200 grams of a product whose specific gravity was 0.9210 at 20°.

This residue, when washed and dried, could not be distilled, even under diminished pressure, without great decomposition and evolution of red nitric fumes, and evidently consisted of nitro-compounds. Not more than 200 cc. of unchanged naphtha was obtained by distilling this oil, and this was readily attacked by fresh acid.

Another portion of the naphtha was treated in the same way, save that the residual oil after each successive treatment with the mixed acids was completely extracted with strong sodium hydroxide to remove nitro-compounds. The nitration was then continued with the residual hydrocarbon. *No limit* could be found to the action of the acid, for the nitration continued up to the very last portion of the naphtha.

145 grams of the naphtha were next treated with nitric acid of specific gravity 1.40 in the same manner as described for the mixed acids, with the following results :

Acid. Grams.	Time. Hours.	Specific gravity of residue at 20°.
150	5	0.820
210	3	0.870
290	2	0.950

The residue amounted to 125 grams of the same nature as that obtained by the action of the mixed acids, and the naphtha, as nearly as could be determined, had been completely converted into these nitro-compounds.

In the same way it was proved that fuming nitric acid and dilute into acid (specific gravity 1.32, 1.23, 1.15) *completely transform* this naphtha into these nitro-products, the action of course varying in speed with the concentration of the acid, the products apparently being the same in each case.

From the results of these preliminary experiments it was evident that the paraffins were readily capable of direct nitration. In view of the great ease with which these nitro-compounds decompose upon distillation, it was determined to work with isolated hydrocarbons, studying the products in each case.

The hydrocarbons which have been used for the experi-

ments herein described are the normal paraffins, hexane, heptane, and octane, from Pennsylvania petroleum. I desire to express my thanks to Dr. C. F. Mabery, of Case School of Applied Science, to whose kindness I am indebted for the material from which hexane was prepared, as well as for the pure heptane. The octane employed was fractioned from the naphtha previously described. In every case, the hydrocarbons have been completely treated with an excess of fuming sulphuric acid, boiled with sodium for several hours, and fractioned over sodium at 1° limits with the aid of Hempel columns, in no case less than twenty times, in one case thirty times, until a constant boiling-point was obtained for each hydrocarbon. Their boiling-points, specific gravity, and other properties have shown their purity.

Hexane, C_6H_{14}.

Normal hexane (boiling-point 68°.5–69°.5) specific gravity 0.6804 at 15°, has been found to be acted upon by fuming nitric acid, by nitric acid of specific gravity 1.42, and by mixed sulphuric and nitric acids, when gently boiled with these acids in an open flask with return condenser, but it is not acted upon to any appreciable extent by acid of greater dilution.

Fuming nitric acid gives the best results, the yield of nitro-products obtained by its use being satisfactory, and the hydrocarbon not being oxidized to any great extent. Usually, a yield of about 20 per cent. of crude nitro-products has been obtained by twenty hours' treatment with this fuming acid, with but little oxidation. But it is difficult, on account of the varying conditions of temperature in an open flask, to obtain concordant quantitative results.

To separate the nitro-products formed by the reaction, the layer of oil is separated from the spent acid, washed with water several times, and dried over calcium chloride. The unchanged hydrocarbon is then distilled off and again treated with more acid. In this way, by several days' successive treatments with fuming nitric acid, *hexane has been completely converted into nitro- and oxidation-products*, the yield of crude nitro-products amounting to perhaps 60 per cent. of the theoretical.

The residues of nitro-compounds left after distilling off the hexane are united and fractioned. Upon the first distillation considerable decomposition results with evolution of nitrogen tetroxide, and a tarry residue is left in the distilling-flask. This has been found to be due to dinitrohexane which cannot be distilled without decomposition. The separate fractions are again distilled, this time with but little or no decomposition.

This method of separation is unsatisfactory and wasteful, in that it destroys the dinitro-hydrocarbons, which usually amount to fully 50 per cent. of the total products. By steam distillation much better results are obtained, the mononitro-hydrocarbon, which is volatile in steam, being completely separated from the dinitro-hydrocarbon, which is not volatile in steam. But the first method was employed for the work herein described.

Nitrohexane, $C_6H_{13}NO_2$.

The distillates of nitro-products of hexane collect almost entirely at 180°–183°.[1] This distillate was thoroughly washed and dried and submitted to analysis.

By Dumas' method, 0.2062 gram substance gave 22.0 cc. (moist) nitrogen at 741 mm. and 23°.

	Calculated for $C_6H_{13}NO_2$.	Found.
N	10.72	10.93

Structure of Nitrohexane.—When treated with potassium hydroxide, potassium nitrite, and then with a few drops of sulphuric acid, it gave the intense red coloration of a nitrolic acid, disappearing with excess of acid, reappearing with the addition of more potassium hydroxide, characterizing it as *primary* nitrohexane.

About 5 grams were reduced to the amine by iron filings and dilute acetic acid, the reduction being complete in about a quarter of an hour. The solution was then made alkaline until sodium hydroxide and the liberated amine distilled off with steam. This hexylamine was a strong base which gave with alcoholic potash and chloroform the isonitrile reaction,

[1] The correct boiling-points, specific gravity, etc., of all these nitro-paraffins is now being investigated.

and with carbon disulphide, alcohol, and solution of mercuric chloride, the mustard-oil reaction characterizing it as a *primary amine*.

Analysis of the platinum double salt gave the following figures :

0.0110 gram substance gave 0.0034 gram platinum.

	Calculated for $(C_6H_{13}NH_3Cl)_2PtCl_4$.	Found.
Pt	30.47	30.90

Properties of Nitrohexane.—Nitrohexane is a light-yellow oil of a peculiar ester-like odor ; insoluble in water, readily soluble in alcohol, ether, etc., very sparingly soluble in aqueous solutions of caustic soda and potash, readily soluble in their alcoholic solutions with a red color.

Dinitrohexane, $C_6H_{12}(NO_2)_2$.

Occasionally, when separating the spent acid from the hydrocarbon, a middle layer has been noticed between the acid and the oil. This compound was separated, washed with water, and dried. Analysis gave the following figures :

By Dumas' method 0.3727 gram substance gave 55.0 cc. (moist) nitrogen at 741 mm. and 21° C.

By combustion, 0.1511 gram substance gave 0.2251 gram CO_2, and 0.0911 gram H_2O.

	Calculated.	Found.
C_6	40.90	40.65
H_{12}	6.82	6.67
N_2	15.91	15.94
O_4	36.37	36.74

These results leave no doubt concerning the composition of the oil.

Structure of Dinitrohexane.—While the quantity obtained was not sufficient to make a determination of its structure possible, there would seem to be no doubt, as its method of formation was exactly similar to that of dinitroheptane and dinitrooctane, that, like the latter, it is a primary nitro-compound, represented by the formula $CH_3(CH_2)_4CH(NO_2)_2$.

Properties of Dinitrohexane.—Dinitrohexane is a clear yellow oil of acid character, sweet, ester-like odor, heavier than

water, sparingly soluble in water, easily soluble in alcohol, ether, etc. It decomposes and carbonizes upon distillation and cannot be solidified by a mixture of ice and salt. It is slowly soluble in concentrated aqueous solutions of sodium and potassium hydroxides, readily soluble in their alcoholic solutions, each solution having an *intense red color*.

Those who, in investigating petroleum, have had occasion to boil their distillates with nitric acid, have noticed upon shaking up these oils with alkalies, after the acid treatment, an intense red coloration. This property of dinitrohexane of turning red with alkalies, characteristic also of dinitroheptane and dinitrooctane, explains this fact, the cause of which was hitherto unknown. The higher primary dinitro-hydrocarbons seem in this respect to resemble the nitrolic acids.

Heptane, C_7H_{14}.

Normal heptane (boiling-point 98°–99°), specific gravity 0.7050 at 15°, behaves toward nitric acid much the same as hexane, but is capable of more rapid nitration, and of nitration by acid of somewhat greater dilution than in the case of hexane.

Nitric acid, of specific gravity 1.42, has been used for the preparation of the mononitro-derivative, the method of nitrating and of separating the products being exactly the same as that described for hexane.

The action of mixed sulphuric and nitric acids yields a considerable amount of dinitroheptane as a middle layer in the nitration flask, and this is easily obtained pure by mechanical separation, washing, and drying of this layer.

As has been stated before, the conditions are not favorable for quantitative comparisons of the rapidity of nitration. But the action of nitric acid, of specific gravity 1.42, gives with heptane as large a yield of nitro-products as is obtained from hexane in the same length of time by the action of fuming nitric acid—that is, about 20 per cent. of the theoretical yield by twenty hours' treatment. And, whereas the formation of dinitrohexane is difficult and the yield small, even by mixed sulphuric and fuming nitric acids, the formation of dinitroheptane is rather easy.

In the case of heptane, as in that of hexane, the hydrocarbon has been completely converted into nitro- and oxidation-products with a yield of perhaps 60 per cent. of crude nitrocompounds. No data have as yet been obtained relative to the time required for this complete conversion, but it does not take as much time as hexane.

Nitroheptane, $C_7H_{15}NO_2$.

The distillates for nitroheptane, collected chiefly at 193°–196°. This distillate, after washing and drying, gave on analysis the following results :

By Dumas' method 0.2242 gram oil gave 20.6 cc. nitrogen at 747 mm. and 18°.

	Calculated for $C_7H_{15}NO_2$.	Found.
N	9.70	10.11

Structure of Nitroheptane.—This nitroheptane gave, with potassium hydroxide, potassium nitrite, and sulphuric acid, the nitrolic-acid test, showing it to be *primary*.

About 3 grams was reduced to the amine by iron filings and dilute acetic acid, the reaction proceeding rapidly. The contents of the flask were then made alkaline with caustic soda and the liberated amine distilled off with steam. Carbon disulphide, alcohol, and mercuric chloride gave, with this amine, the mustard-oil reaction, and chloroform, alcohol, and caustic potash the isonitrile reaction, showing the amine to be *primary*.

The chlorplatinate was formed. Analysis of this compound showed it to be impure.

0.0456 gram substance gave, on ignition, 0.0155 gram platinum.

	Calculated for $(C_7H_{15}NH_3Cl)_2PtCl_4$.	Found.
Pt	29.82	33.98

It was noticed that too vigorous reduction of these nitroparaffins resulted in partial decomposition and the formation of some ammonia, gentle reduction giving the amines. It is probable that some ammonium chlorplatinate was contained in the compound analyzed, thus accounting for the high percentage of platinum.

Properties of Nitroheptane.—Nitroheptane, in all its properties so far observed, resembles nitrohexane very closely. It could not be solidified by ice and salt, and could be distilled without decomposition. It has much the same peculiar, ester-like odor as nitrohexane, and its solubility is the same.

Dinitroheptane, $C_7H_{14}(NO_2)_2$.

This compound, separated and purified in the same way as dinitrohexane, gave the following analytical results :

By Dumas' method, 0.1421 gram substance gave 18.4 cc. nitrogen at 738 mm. and 20° C.

	Calculated for $C_7H_{14}N_2O_4$.	Found.
N	14.74	14.37

Structure of Dinitroheptane.—As a dinitroparaffin, dinitroheptane should, on reduction, yield heptoic acid, hydroxylamine, and ammonia, according to the well-known reaction of this class of compounds,

$$RCH(NO_2)_2 + 8H = RCHO + 2H_2NOH + H_2O,$$
$$RCHO + NH_2OH = RCOOH + NH_3,$$
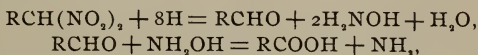
and this has been found to be the case.

About 5 grams of the dinitroheptane was reduced by means of tin and hydrochloric acid. The solution was diluted with water to about a liter, and then distilled in steam. The distillate thus obtained contained a very small quantity of a fatty acid, mixed with a small quantity of some neutral compound, probably an aldehyde. This fatty acid gave a characteristic insoluble copper salt but there was not sufficient for a quantitative determination. The solution left in the distilling-flask reduced Fehling's solution, showing the presence of hydroxylamine. This solution was then made alkaline with sodium hydroxide and distilled in steam, the odor of ammonia being apparent in the distillate. This distillate was evaporated to a small volume after acidifying with hydrochloric acid, and the double platinum salt formed. Analysis of this salt gave the following results :

0.3735 gram substance gave, on ignition, 0.1617 gram of platinum.

	Calculated for $(NH_4Cl)_2PtCl_4$.	Found.
Pt	43.92	43.30

Another attempt was made to obtain the heptoic acid by reducing about 5 grams of the dinitroheptane with tin and hydrochloric acid, diluting to about a liter, and extracting with ether. The ether was distilled off, the residue diluted with about a liter of water, and boiled with an excess of silver carbonate. The filtrate deposited, on evaporation and cooling, a very few crystals, but not sufficient for a determination of silver. But the formation of the hydroxylamine and ammonia indicates that the dinitroheptane is primary, represented by the formula $CH_3(CH_2)_5CH(NO_2)_2$.

Properties of Dinitroheptane.—Dinitroheptane is a clear, yellow oil, resembling dinitrohexane, but is less soluble in water than the latter. It has a similar, ester-like odor, and could not be solidified by a freezing-mixture of ice and salt. It decomposes by distillation and turns deep-red with alkalies.

Octane, C_8H_{18}.

Normal octane (boiling-point 124°–125°, specific gravity 0.7260 at 15°), when gently boiled with fuming nitric acid, of specific gravity 1.52, is acted upon violently, and much oxidation of the hydrocarbon results. Nitric acid, of specific gravity 1.42, and mixed sulphuric and nitric acids, react readily, without much oxidation of the hydrocarbon. Acid of greater dilution, even that consisting of one part nitric acid to four parts water, also acts upon the hydrocarbon, the action of course becoming slower the greater the dilution of the acid employed, but with the formation of the same products in every case, and the hydrocarbon is finally completely converted into nitro- and oxidation-products.

For the preparation of mononitrooctane, nitric acid of specific gravity 1.42 gives the best results, the action of the mixed acids resulting, as in the case of heptane, in the formation of considerable quantities of the dinitro-hydrocarbon. By employing either the 1.42 acid alone or the mixed acids, complete conversion of the hydrocarbon into nitro- and oxidation-products has been obtained in *eighteen to twenty hours*, with a

yield of 60 or 70 per cent. of the theoretical quantity of nitro-compounds.

For the separation of the products the same method was employed as for those of hexane and heptane. In fractioning the mononitrooctane the same decomposition was noted upon first distillation as in the case of hexane and heptane, and this also has been found to be due to the dinitro-hydrocarbon.

Nitrooctane, $C_8H_{17}NO_2$.

The fractions for nitrooctane collected chiefly at 205°–210°, with some decomposition. A nitrogen determination in this fraction gave the following result:

By Dumas' method, 0.3938 gram substance gave 32.4 cc. (moist) nitrogen at 742 mm. and 22° C.

	Calculated for $C_8H_{17}NO_2$.	Found.
N	8.83	8.86

Structure of Nitrooctane. — With potassium hydroxide, potassium nitrite, and sulphuric acid, nitrooctane gave the nitrolic-acid test, characterizing it as *primary.*

About 5 grams was reduced to the amine by iron filings and acetic acid, the solution made alkaline with sodium hydroxide, and distilled in steam. The liberated amine gave both the isonitrile and the mustard-oil reaction, proving it to be primary.

Analysis of the double salt of platinum chloride and the octylamine gave the following figures:

0.1167 gram gave, on ignition, 0.0342 gram platinum.

	Calculated for $(C_8H_{17}NH_3Cl)_2PtCl_4$.	Found.
Pt	29.20	29.32

Still further evidence that the nitrooctane is primary, is afforded by the fact that it agrees in every respect with the primary nitrooctane made by Eichler[1] from octyl iodide and silver nitrite. It is a light-yellow liquid of ester-like odor, partially decomposing upon distillation, and resembling nitro-hexane and nitroheptane in its solubility and other properties.

[1] Ber. d. chem. Ges., **12**, 1883.

Dinitrooctane, $C_8H_{16}(NO_2)_2$.

Dinitrooctane was obtained by the action of mixed sulphuric and nitric acids upon octane, as a middle layer in the nitration-flask. After washing and drying, analysis gave the following results:

By Dumas' method, 0.3964 gram substance gave 46.0 cc. nitrogen at 750 mm. and 15° C.

By combustion, 0.4884 gram substance gave 0.8469 gram CO_2, and 0.3559 gram H_2O.

	Calculated.	Found.
C_8	47.06	47.27
H_{16}	7.84	8.08
N_2	13.73	13.63
O_4	31.37	31.02

Structure of Dinitrooctane.—To determine the structure of dinitrooctane it was reduced with tin and hydrochloric acid. If primary, octoic acid, hydroxylamine, and ammonia should be the products, and this was found to be the case.

About 5 grams of the oil were reduced with tin and hydrochloric acid, diluted with water to about 1 liter, and distilled in steam. A considerable amount of the fatty acid distilled with the steam. The silver salt of this acid was formed and analyzed.

0.1360 gram substance gave 0.0785 gram AgCl.

	Calculated for $C_7H_{16}COOAg$.	Found.
Ag	43.01	43.38

The residue in the distilling-flask reduced Fehling's solution rapidly, showing presence of hydroxylamine. This residue was made alkaline with sodium hydroxide and distilled in steam. The distillate, smelling strongly of ammonia, was acidified with hydrochloric acid, and the chlorplatinate formed. Analysis of the latter gave the following figures:

I. 0.2807 gram substance gave, on ignition, 0.1222 gram platinum.

II. 0.4885 gram substance gave, on ignition, 0.2137 gram platinum.

	Calculated for $(NH_4Cl)_2PtCl_4$.	Found. I.	II.
Pt	43.92	43.54	43.75

Hence the dinitrooctane is primary, and is represented by the formula $CH_3(CH_2)_6CH(NO_2)_2$.

Properties of Dinitrooctane.   Dinitrooctane is a clear, yellow oil of peculiar odor, somewhat heavier than water ; it cannot be solidified by a mixture of ice and salt.   It is turned intensely red by alkalies and resembles dinitrohexane and dinitroheptane in all of its observed properties.

Oxidation-products.

As mentioned before, the action of nitric acid upon these hydrocarbons is one of oxidation as well as of nitration.   For the study of the oxidation-products, the hydrocarbon remaining after several nitrations was employed in each case, in order to preclude, as far as may be, the possibility of the presence of hydrocarbons other than the paraffins.   This hydrocarbon was again treated with nitric acid of the desired concentration until the acid was exhausted, the spent acid neutralized with sodium carbonate, evaporated to dryness, and the salts examined.

The results of many experiments with hexane, with heptane, and with octane, with the employment of various concentrations of acid, has been to show that the same oxidation-products result from each hydrocarbon and from each concentration of acid.   The work of Schorlemmer[1] and of Beilstein and Kurbatow[2] had indicated the probability of this result.

These oxidation-products are :

1.   *Carbonic Acid.*—Determined in the escaping gases of the nitration-flask by its precipitation of solutions of calcium and barium hydroxides.

2.   *Acetic Acid.*—Detected in the salts from the spent acid by its ethyl ester and its behavior with ferric chloride.

3.   *Succinic Acid.*—Determined by precipitation with ammoniacal barium chloride and with ferric chloride in the cold.

4.   *Oxalic Acid.*—Determined by the properties of its calcium and silver salts.

The formation of the first three products has been noted before by other investigators.   Schorlemmer,[2] however, stated that no oxalic acid was formed by the oxidation of hexane,

[1] *Loc. cit.*   [2] *Loc. cit.*   [3] *Loc. cit.*

octane, or diamyl by nitric acid. Although numerous qualitative tests seemed to show that oxalic acid was present in each case, a quantitative determination was made for the purpose of furnishing definite proof.

The salts obtained by oxidation of heptane with 1.35 nitric acid for sixteen hours were dissolved in water, the succinic acid removed by boiling with ferric chloride and excess of sodium acetate, and oxalic acid precipitated in the filtrate by calcium acetate. The precipitate was filtered, washed, and dried, and the calcium determined.

0.0480 gram substance gave, on ignition, 0.0247 gram CaO, and this gave 0.0511 gram $CaSO_4$.

	Calculated for CaC_2O_4.	Found.
Ca	31.25	31.45

This proves the presence of oxalic acid. A blank experiment showed the reagents to be free from oxalic acid. The total amount formed in this case by boiling 97 grams heptane with 1.35 nitric acid for sixteen hours was only 0.04 per cent.

Carbonic acid is by far the most abundant oxidation-product. The quantity of the other oxidation-products formed by two days' boiling of the hydrocarbons with nitric acid, does not exceed 2 per cent.

These results seem to me to prove conclusively that the paraffins are rather readily capable of direct nitration. No trace of secondary or of tertiary nitro-compounds has been observed in these products, and this seems noteworthy, showing as it does that while, according to Konowalow, the normal paraffins give *only secondary* nitro-hydrocarbons when nitrated in sealed tubes, *only the primary* nitroparaffins are formed by nitration in an open vessel.

The dinitro-hydrocarbons are most probably formed by further nitration of the mononitro-hydrocarbons, and it is possible that the oxidation-products noted may be due to further action of the acid on one or both of these nitro-compounds. This will be investigated.

As this appears to be the first instance of the formation of primary nitroparaffins by direct nitration, and as only a very few of these higher nitroparaffins have ever been prepared in

any way, the investigation is being continued. At present, experiments are in progress upon the nitration of the normal paraffins, hexane, heptane, octane, and nonane, with a study of the nature and properties of the nitro- and oxidation-products. The investigation will be extended so as to include other normal and isohydrocarbons, and an endeavor will be made to obtain data relative to the speed of the reaction and to the yield.

ON THE SILVER SALT OF 4-NITRO-2-AMINOBENZOIC ACID AND ITS BEHAVIOR WITH ALKYL AND ACYL HALIDES.

BY H. L. WHEELER AND BAYARD BARNES.

It is well known, from the work of Griess,[1] Lauth,[2] Michler,[2] Michael,[4] and others, that the alkali salts of the aminobenzoic acids do not give esters directly with alkyl halides, but that the alkyl groups attach themselves entirely or partially to nitrogen. In this respect the sodium salts of the acyl amides and those of the aminobenzoic acids are analogous.

The silver salts of the amides, however, behave differently;[5] here a replacement of the metal takes place and oxygen esters result, while the formation of nitrogen derivatives in this case has not been observed.

The action of alkyl and acyl halides on the silver salts of the aminobenzoic acids has, apparently, not been investigated, and it was with the object of investigating this action that the present work was undertaken. It seemed of interest to determine whether these silver salts behave like the silver salts of the amides and anilides or whether, like the sodium compounds, the entering groups attach themselves to nitrogen.

The new 4-nitro-2-aminobenzoic acid was selected as its esters are solids. We have found that the silver salt of this acid gives—as the chief product—with ethyl iodide in molecu-

[1] Ber. d. chem. Ges., **5**, 1038.   [2] Bull. Soc. Chim. (Paris), [3], **9**, 970.
[3] Ber. d. chem. Ges., **9**, 401.   [4] This JOURNAL, **7**, 198.
[5] Comstock and Kleeburg : This JOURNAL, **12**, 493, and **13**, 514 ; Tafel and Enoch : Ber. d. chem. Ges., **23**, 104 and 1554.

lar proportions, 4-nitro-2-ethylaminobenzoic acid; the ethyl group attaching itself to nitrogen, and, next, in smaller quantity, 4-nitro-2-ethylaminoethyl benzoate is formed, while no 4-nitro-2-aminoethyl benzoate was observed.

The behavior of the silver salt with ethyl iodide is therefore analogous to that of the above-mentioned sodium compounds. In this connection it may be remarked that Kraut[1] found that the silver salt of aminoacetic acid does not give the simple ester with ethyl iodide, when these compounds are used in molecular proportions, but the triethyl derivative of the ester and in the same manner betaïn methyl ester results.

On the other hand Curtius[2] found that the methyl and ethyl esters of acetyl glycin result from the silver salt, therefore the metal in this salt is directly replaceable. We have found, precisely in accordance with this, that if 4-nitro-2-aminobenzoic acid is acetylated, then both the sodium and silver salts give oxygen derivatives.

The action of acyl chlorides on the silver salt of anthranilic acid and on 4-nitro-2-aminobenzoic acid might lead to the formation of mixed anhydrides analogous to the action of acetyl chloride on sodium benzoate.[3] We have found, however, that in the presence of the amino group the acyl group attaches itself entirely to nitrogen. A similar result was observed in the case of aminoacetic acid by Kraut,[4] Hartmann,[5] and Curtius.[6] They prepared acetylaminoacetic acid from the silver salt of glycin and acetyl chloride, and Curtius showed that hippuric acid is thus formed. The silver salts of the anilides also give nitrogen derivatives with acyl halides.[7]

The sodium salts of the amides were formerly universally represented as having the metal attached to nitrogen, since they give nitrogen alkyl compounds with alkyl halides. As shown here, the silver salt of the aminobenzoic acids, which contain the metal joined to oxygen, nevertheless, give nitrogen derivatives with ethyl iodide, etc., and silver is generally more readily replaceable than sodium. It is shown from this, as has frequently been suggested, that the position of the

[1] Ann. Chem. (Liebig), **182**, 172.   [2] Ber. d. chem. Ges., **17**, 1672.
[3] Gerhardt: Ann. Chem. (Liebig), **87**, 81.   [4] *Loc. cit.*
[5] Ann. Chem. (Liebig), **133**, 105.   [6] J. prakt. Chem. [2], **26**, 170.
[7] Wheeler and Boltwood: This JOURNAL, **18**, 381.

metal in the salts of the amides cannot be determined by the structure of the reaction product, and that the sodium salts of the amides may leave the metal joined to oxygen. If now, with this view, we arrange the salts of the amino and acet-amino acids with those of the amide, according to their behavior with alkyl halides, we have the following :

$$\text{I.} \quad \begin{array}{c} NH_2 \\ | \\ CH_2CO_2Ag[Na] \end{array} \qquad \begin{array}{c} NH_2 \\ | \\ C_6H_4CO_2Ag[Na] \end{array} \qquad \begin{array}{c} NH \\ \| \\ RCONa \end{array}$$

$$\text{II.} \quad \begin{array}{c} NHCOCH_3 \\ | \\ CH_2CO_2Ag \end{array} \qquad \begin{array}{c} NHCOCH_3 \\ | \\ C_6H_4CO_2Ag \end{array} \qquad \begin{array}{c} NH \\ \| \\ RCOAg. \end{array}$$
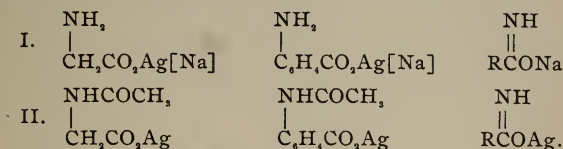
The fact that the first series give nitrogen derivatives is explained by the positive character of the amido and imido groups ; here the alkyl halide reacts by addition to the nitrogen, there being a subsequent separation of hydrogen halide, or, in the case of the amides, of sodium halide.

In the second series either these groups or the molecules are more negative and additions to the nitrogen do not take place, but instead the metal is replaced by alkyl.

The above affords further data for and confirms the conclusion of Nef, Hantzsch,[1] Freer and Sherman,[2] and others, that the sodium in the salts of the amides and anilides is joined to oxygen. The amides and anilides, in general, have the normal structure, while the salts, with the possible exception of the mercury compounds, are derivatives of the pseudoform and contain the imido group. It is certain that most if not all the reactions of these compounds involve, as the first step, addition. These unstable addition-products then decompose into more stable derivatives, which latter constitute the products that are isolated.

Experimental Part.

4-*Nitro-2-acetaminobenzoic Acid,* $C_6H_3 \begin{cases} CO_2H & (1) \\ NHCOCH_3 & (2). \\ NO_2 & (4) \end{cases}$—
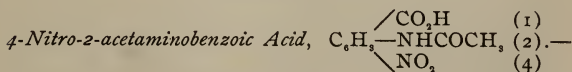
This acid was prepared by oxidizing 4-nitro-2-acettoluide with a 1 per cent. solution of potassium permanganate. The operation being essentially the same as that employed by

[1] Ann. Chem. (Liebig), **296**, 91.   [2] This JOURNAL, **18**, 570.

Bedson[1] in oxidizing orthoacettoluide. Bedson obtained a yield of only 32 per cent. of acetylorthoaminobenzoic acid. Apparently the nitroacettoluide is oxidized more smoothly since we have obtained yields varying from 44 to 77 per cent. of the calculated. The best yield is obtained when the quantity of toluide employed does not exceed 50 grams. On filtering, concentrating, and acidifying the solution after oxidizing, the acid separates as a yellowish-white precipitate. It crystallizes from alcohol in long, light yellow needles, which melt at about 215°. A nitrogen determination gave :

	Calculated for $C_9H_8N_2O_5$.	Found.
N	12.5	12.4

It was observed that acids saponify this acetyl compound more readily than alkali.

The sodium salt was obtained as a bright yellow precipitate by adding one molecule of sodium ethylate to an absolute alcohol solution of the acid. It is readily soluble in water and somewhat in alcohol.

The silver salt is precipitated in a bright yellow, gelatinous form when silver nitrate is added to an aqueous solution of the sodium salt. It was found best to make the precipitation at a temperature of about 70°, then, on stirring vigorously, the precipitate becomes granular and is more readily filtered. It can be dried at 100° and is quite stable when exposed to light.

	Calculated for $C_9H_7N_2O_5Ag$.	Found. I.	II.
Ag	32.6	32.35	32.31

Ethyl 4-nitro-2-acetaminobenzoate was prepared by heating the above sodium salt with an excess of ethyl iodide in a sealed tube at about 190° for eight hours. The product was extracted with water and then crystallized from alcohol and finally from ligroïn, when it melted at 112°. It forms bright yellow plates or flattened prisms. This compound is more readily formed, however, from the silver salt. A nitrogen determination in a product thus obtained gave :

[1] Jour. Chem. Soc., 1880, 752.

	Calculated for $C_{11}H_{12}N_2O_5$.	Found.
N	11.11	10.77

When this compound is treated with cold sodium hydroxide the ethyl group is removed, leaving the acetyl group unaffected; on the other hand, when it is warmed with sulphuric acid, in alcoholic solution, the acetyl group alone is removed.

4-Nitro-2-aminobenzoic Acid.—This was best obtained by warming the acetyl compound in alcohol with acids. It separates from alcohol in long, bright-red needles. On heating it begins to darken at 260°, and then melts with decomposition at 264°. A nitrogen determination gave :

	Calculated for $C_7H_6N_2O_4$.	Found.
N	15.38	15.29

The ammonium salt was formed when dry ammonia gas was passed into an ethereal solution of the acid. It dissolves readily in water.

	Calculated for $C_7H_9N_3O_4$.	Found.
NH_3	8.58	8.49

The sodium salt was obtained as a bright-red precipitate when one molecular proportion of sodium ethylate was added to the alcoholic solution of the acid. It is quite soluble in water and sparingly in alcohol.

The silver salt was obtained as a pink, gelatinous precipitate when the above sodium salt was dissolved in water and the requisite amount of silver nitrate was added. On warming to about 50° and stirring, it coagulates to a tan-colored powder. The yield corresponds to the calculated.

	Calculated for $C_7H_5N_2O_4Ag$.	Found.
Ag	37.37	37.30

On treating this salt, suspended in ether, with the calculated quantity of acetyl chloride, enough heat was liberated to cause the solution to boil. It was warmed until the odor of acetyl chloride disappeared, then filtered, and evaporated over potassium hydrate in a vacuum desiccator. The crystals that separated proved to be 4-nitro-2-acetaminobenzoic acid.

Methyl 4-nitro-2-aminobenzoate, obtained by boiling the acid with methyl alcohol and sulphuric acid, melts at 157°. It is

soluble in ligroïn and alcohol and separates in dark, orange-colored clusters of needles.

	Calculated for $C_8H_8N_2O_4$.	Found.
N	14.28	14.15

Ethyl 4-nitro-2-aminobenzoate was obtained by boiling the acid with alcohol and hydrogen chloride. It forms dark, orange-colored plates, which are quite soluble in alcohol and benzene.

	Calculated for $C_9H_{10}N_2O_4$.	Found.
N	13.33	13.38

4-Nitro-2-ethylaminobenzoic Acid.—This was the chief product formed when the silver salt of the amino acid was suspended in ether and warmed with the calculated quantity of ethyl iodide for three days, the reaction then being practically complete. The ethereal solution was evaporated and the residue treated with dilute sodium hydroxide; on filtering and acidifying the alkaline solution, this compound separated as a bright yellow precipitate. On crystallizing from alcohol and benzene it separated in the form of golden-yellow plates, which melt at about 223°. A nitrogen determination gave:

	Calculated for $C_9H_{10}N_2O_4$.	Found.
N	13.33	13.48

Ethyl 4-nitro-2-ethylaminobenzoate.—The part insoluble after the above treatment with alkali proved to be this diethyl derivative. It is formed in smaller quantity than the nitrogen monoethyl derivative. From benzene and alcohol, in which it is very soluble, it separates in the form of long, pale-yellow needles; these melt at 80°.

This compound was also formed when 4-nitro-2-ethylaminobenzoic acid was boiled with alcohol and sulphuric acid; an analysis therefore seemed superfluous.

Acetylorthoaminobenzoic acid was obtained when the silver salt of anthranilic acid was treated with acetyl chloride. It forms white prisms melting at 185°, as observed by Döbner and `Miller.[1]

NEW HAVEN, CONN.,
January, 1898.

[1] Ber. d. chem. Ges., **15**, 3077.

FORMAMIDE AND ITS SODIUM AND SILVER SALTS.

By Paul C. Freer and P. L. Sherman, Jr.

In continuing our work on the various derivatives of formic acid with a view to determining the constitution of the formyl group, it was found necessary to use pure formamide. The various methods for its preparation were therefore carefully tried. A. W. Hofmann,[1] Behrend,[2] Lorin,[3] and Basarow[4] have all contributed methods, the details of which are more or less carefully described. The latter two methods need not be commented upon here, as no attempt was made to secure pure formamide. Hofmann digested dry ethyl formate with dry ammonia and heated the product in sealed tubes for two days, at 100°. The ammonium formate formed was then distilled. Behrend first heated ammonium formate with urea, and then distilled the product in a partial vacuum. The analyses given are as follows :

	Hofmann.	Behrend.	Calculated for $HCONH_2$.	Calculated for $HCOOH$.	Calculated for NH_4CN.	Calculated for $HCOONH_4$.
C	27.61	26.43	26.67	26.08	27.27	19.04
H	6.71	6.89	6.67	4.34	9.09	7.93
N	....	30.87	31.11	....	63.63	22.22

In order to see if these analyses denoted pure products, the distillation of both ammonium formate and pure formamide at ordinary pressure and in a partial vacuum was carefully studied and the following results noted :

When ammonium formate is heated in a distilling-flask, water and ammonia begin to distil at about 100°, both products continuing to increase as the temperature slowly rises. At 150° the distilling liquid contains noticeable amounts of formic acid, and these continue to increase up to the temperature of about 185°–190°, when formamide begins to pass over, and from this time on forms the leading product.

Between 180°–200°, however, three side reactions occur, which not only lower the yield of formamide but render it impossible to make pure formamide according to this method.

[1] Jour. Chem. Soc. [2], 1-72.　　　[2] Ann. Chem. (Liebig), 128, 335.
[3] Compt. rend., 59, 51.　　　[4] Ber. d. chem. Ges., 4, 409.

The first reaction referred to is the dissociation of the ammonium formate, which is still undecomposed in the distilling-flask, into formic acid and ammonia. The ammonia is given off as a gas and the formic acid distils over. If care is taken to provide the flask with a long water condenser, the formic acid will, to a large part, unite with the ammonia while on the way to the receiver, often in such quantities as entirely to stop the tube of the condenser. When only an air condenser is used, the tube soon becomes hot enough to prevent the crystallization of the ammonium formate, and it passes into the receiver as a thick, colorless liquid, not to be distinguished from the formamide which distils at the same time.

Besides this dissociation of the ammonium formate, which seems to have been overlooked, there is a second side reaction, noticed by Hofmann, according to which formamide decomposes into carbon monoxide and ammonia while undergoing distillation. The third side reaction is the decomposition of formamide into prussic acid and water. This latter reaction takes place mostly after the temperature of the distilling vapors has reached 195°. The prussic acid unites to some extent, as did the formic acid, with the ever-present ammonia and is found in the distillate as ammonium cyanide; the water unites with the formamide in the receiver to form ammonium formate.

The products of distillation of ammonium formate under ordinary pressure are, therefore, water, ammonia, formic acid, formamide, ammonium formate, carbon monoxide, prussic acid, and ammonium cyanide. These products taken together give the distillate an acid reaction, and vary decidedly in their proportions according to the rate of distillation, the kind of condenser used, and the amount of ammonium formate distilled. Even in fractions having an almost constant boiling-point, the presence of two or more of the above-mentioned products could be easily proved. Analyses of these fractions gave percentages for carbon, hydrogen, and nitrogen agreeing well with those for formamide. The reason for this, however, is seen by a study of the percentages calculated for formic acid, ammonium formate, and ammonium cyanide, and given in the table above.

The attempt was then made to purify the distillate by distillation in a vacuum. It was found that while the decomposition of formamide was prevented to a larger extent, the dissociation of the ammonium formate took place more readily than at ordinary pressure, and at a temperature so nearly that at which the formamide distilled, that no separation could be effected in this way.

In order to insure the complete decomposition of ammonium formate into water and formamide, and at the same time to prevent the dissociation of ammonium formate and the decomposition of formamide, the following process was tried with good results: Pure formic acid was neutralized with concentrated ammonia, and the half-solid mass poured into a distilling-flask, and heated about two hours at a temperature beginning at 100° and increasing gradually to 180°. The dissociation of the ammonium formate was prevented by means of dry ammonia gas, which was run in constantly until the decomposition was complete and no more water distilled over even at a temperature of 180°. The ammonia was dried over stick alkali and metallic sodium wire, and acted as a dehydrating agent while it prevented effectually the dissociation of the ammonium formate. When the current of ammonia was stopped, even momentarily, the dissociation of the ammonium formate began at once. The vapors of formic acid filled the distilling-flask and began to distil over. With the introduction of new ammonia gas the formic acid was neutralized, and the ammonium formate was deposited in feathery crystals on the cool sides of the flask and condenser.

When the decomposition of the ammonium formate was complete, the resulting amber-colored, heavy, oily liquid was cooled in the current of ammonia, and then fractioned in an atmosphere of ammonia under a pressure of about one-half mm., which insured the minimum amount of decomposition. A large U-tube, filled with pumice stone and concentrated sulphuric acid, was introduced between the receiver and the pump, and after the excess of ammonia had passed over, no more gas was observed to pass through the sulphuric acid. The first portions of the distillate were discarded, to be

worked up again. The rest of the distillate, which boiled at 85°–95°,[1] was perfectly colorless, oily, possessed a high index of refraction, reacted neutral towards litmus, and when kept well stoppered, as it is very hygroscopic, did not decompose, even after months of summer weather.

At —1° it solidifies to a white crystalline mass of long, irregular needles. When even small quantities of ammonium formate are present, or any other impurity, in fact, the melting-point of formamide is very much lowered.

The specific weight of formamide, taken at 4°, was found to be 1.16. The specific weight for acetamide is given by Mendius as 1.12,[2] and for propionamide, by Schroeder,[3] as 1.03.

Formamide dissolves in water in all proportions without decomposition at first; even dilute alkali does not decompose it at 0°. At room temperature it gives off ammonia at once.

When distilled at ordinary pressure, it begins to decompose at 100°, giving off ammonia, carbon monoxide, prussic acid, and water. No liquid distillate passes over under 200°, the first that appears being dark amber in color, which darkens on standing. The rest of the distillate was colorless at first, but gradually darkened. The entire product distilled between 203°–216°. In the distillate water, ammonia, and prussic acid were found. Crystals of ammonium formate were seen at the beginning of the distillation on the sides of the condenser.

Sodium Formamide.—This compound was prepared as previously described,[4] pure formamide being used in its formation. It was found to be quite stable when pure, although decomposing at once under the influence of either heat or moisture. Organic halogen compounds, such as ethyl iodide, acetyl chloride, or benzoyl chloride, could not be made to react with it.

Dissolved in absolute alcohol, it gives a pure white, curdy precipitate when brought in contact with alcoholic silver

[1] The boiling-point under this pressure, can be given only approximately, as almost imperceptible changes in the pressure made large variations in the boiling-point.

[2] Beilstein [III],ʼi, 1236.　　　　[3] Ber. d. chem. Ges., **12**, 562.

[4] This JOURNAL, **18**, 580.

nitrate. This silver compound is very sensitive to both light and heat, and darkens quickly, depositing a mirror of metallic silver.

Titherly,[1] in his work on sodamide, prepared the sodium salts of several acid amides in a new way, by allowing sodamide to react on the acid amide while suspended in boiling benzene, until the evolution of ammonia ceased. The sodium salts thus prepared were white crystalline powders, and in other ways corroborated the work already done on these bodies.[2] The yield, in every case given, was described as being theoretical, though no method for removing the excess of either the sodamide or the acid amide was given.

However, when these sodium salts were dissolved in absolute alcohol and treated with alcoholic silver nitrate, they all gave brightly colored precipitates ; with formamide, orange-red ; with acetamide, bright orange-red ; with propionamide, orange ; and with benzamide, orange-brown. Titherly sought to explain the difference in the color between the silver salts prepared by himself and those prepared by others[3] by assigning to his the constitution R—CO—NHAg, and to the other the constitution R—C(OAg)=NH. In view of the fact, however, that we prepared a white silver formamide in exactly the same manner as Titherly prepared his colored salt, it might be supposed that there were two kinds of sodium salts of the acid amides before us.

To disprove the correctness of this assumption we prepared sodium formamide according to the method given by Titherly.[4] The theoretical quantities of sodamide and formamide, the latter being in slight excess, were suspended in dry benzene and boiled for two hours. A small part of the white powder, which had precipitated, was taken out, dissolved in absolute alcohol, and added to alcoholic silver nitrate. The precipitate which formed was bright orange in color. After another hour's steady boiling, however, the reaction-product gave a pure white precipitate with silver nitrate, which

1 Jour. Chem. Soc., **72**, 460.

2 Titherly describes sodium formamide as if it were a new substance. He apparently overlooked our work of the previous year. See also Curtius : Ber. d. chem. Ges., **23**, 3039; Blacher : *Ibid*, **28**, 432 and 2352.

3 Tafel and Enoch : Ber. d. chem. Ges., **23**, 104 ; Beilstein [III], **1**, 1237.

4 Jour. Chem. Soc., **72**, 467.

quickly blackened on exposure to light and heat, and was therefore identical with the silver formamide prepared by us. As sodamide, even in very dilute solutions, gives a bright-orange precipitate with silver nitrate, it is probable that this substance was present in the sodium formamide at the time it was tested by Titherly, and hence caused the colored precipitate, rather than that the longer heating changed the sodium salt first formed into its desmotropic form.

As a further proof that unchanged sodamide was always present in those sodium salts which gave colored silver precipitates, sodium acetamide, prepared according to Titherly's directions, was decomposed with ice-water, to which some Nessler's reagent had been previously added. A yellow color, that appeared after a few moments, denoted the presence of ammonia, and hence indicated the decomposition of sodamide, while sodium acetamide, prepared according to Blacher, gave no test for ammonia even after an hour's standing.

The above experiments lead to the conclusion, therefore, that so far only one series of sodium and silver salts of the acid amides has been found, and that the silver compounds are all white, easily decomposable bodies.

Concerning the constitution of these bodies, as well as of the sodium compounds from which they were made, further evidence is necessary. From the experiments made by Blacher,[1] Comstock and Wheeler,[2] Tafel and Enoch,[3] and others,[4] they conclude that in the sodium amide bodies the sodium is attached directly to the nitrogen, while in the silver compounds, on the other hand, the silver is attached to oxygen. The reactions which they carried out with the higher aliphatic and the aromatic acid amides do not succeed with sodium and silver formamide. That the latter need not be assigned another constitution on this account, is evident, for this indifference in the reactivity of the sodium and silver atoms is probably due to the peculiar nature of the formyl group. The arguments of Titherly, based upon the different color of his silver compounds have, in view of the above work, no value.

ANN ARBOR, January, 1898.

1 Blacher: Ber. d. chem. Ges., **28**, 432, 2352.
2 Comstock and Wheeler: This JOURNAL, **13**, 514.
3 Enoch and Tafel: Ber. d. chem. Ges., **23**, 104.
4 Wheeler and Walden: This JOURNAL, **19**, 129.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

XIII.—A STUDY OF THE REACTION OF THE DIAZOPHENOLS AND OF THE SALTS OF CHLOR- AND BROMDIAZOBENZENE WITH ETHYL AND WITH METHYL ALCOHOL.[1]

By Frank Kenneth Cameron.

The special investigation, the results of which are here recorded, was on the influence of the hydroxyl group, and the elements chlorine and bromine, when substituted in the benzene nucleus, in determining the decomposition of diazo compounds with ethyl and methyl alcohols.

The decomposition of these compounds with water[2] has been studied; it takes place normally, and it does not seem desirable, in this connection, to do more than refer to these investigations for the sake of completeness.

The Diazo Phenols.

Ample quantities of ortho- and paramidophenol hydrochlorates were at my disposal, and I was especially fortunate in having a kilogram of the free base, metamidophenol, available for this research.

Paradiazophenol chloride was prepared by the method of Schmidt.[3] The paramidophenol hydrochlorate was finely pulverized in an agate mortar, and then poured into a beaker containing a saturated solution of nitrous oxide in alcohol, and surrounded by a freezing-mixture of crushed ice and hydrochloric acid. The mixture was stirred for about five minutes, then allowed to settle for a few minutes, and carefully decanted, so as to leave any undissolved amido salt. The solution rapidly became dark-blue. On the addition of much ether, and strongly cooling, the diazo compound separated in fine white crystals, which were filtered off with the aid of a pump, and dried on bibulous paper. It soon decom-

[2] Ber. d. chem. Ges., 1, 67; 5, 777; 7, 905; 9, 1160; 11, 1161; 8, 362; Ann. Chem. (Liebig), 176, 30-45.

[3] Ber. d. chem. Ges., 1, 68.

posed in the air, gradually becoming a bright crimson in color. Heated on platinum foil, it decomposed, with formation of violet fumes, much resembling in appearance iodine vapor, and left no residue when freshly prepared.

20 grams of the diazo compound, with 150 cc. ethyl alcohol, was placed in a flask fitted with an inverted condenser, and slowly warmed. Decomposition commenced at once, the solution becoming reddish-brown, a gas being given off, and a strong odor of aldehyde perceived. The decomposition appeared completed in about an hour. The alcohol was then distilled off, the residue distilled with steam, and the distillates examined. As nearly as I could determine, the hydrogen reaction alone took place. Undoubtedly, phenol was formed in considerable quantity, and was identified by precipitating with bromine water, recrystallizing the precipitate, tribromophenol, and determining its melting-point. There was no evidence of any other definite decomposition-product. A considerable tarry residue remained after the distillation. This was examined, and attempts made to extract something definite with ether, benzene, ligroïn, chloroform, glacial acetic acid, acetone, etc., but without success.

20 grams of the diazo compound was treated with 150 cc. methyl alcohol. Decomposition commenced on warming, but not so readily as in the last experiment, the diazo salt, in the earlier part of the experiment, crystallizing, to some extent, in beautiful, shell-like aggregates on the sides of the flask. The decomposition was completed in about one and one-half hours. After distilling with steam, the distillate was examined, phenol identified, but no other definite product could be isolated.

Weselsky and Schuler,[1] studying the action of water on paradiazophenol chloride, found the reaction was cleaner in the presence of a dilute acid.

Therefore, 20 grams of the diazo compound was treated with ethyl alcohol, containing 20 per cent. sulphuric acid. The decomposition was somewhat slower and cleaner. Phenol and aldehyde were the only products that could be identified.

20 grams of the diazo compound was then decomposed in

[1] Ber. d. chem. Ges., **9**, 1160.

ethyl alcohol, saturated with hydrochloric acid, a stream of the dry gas being constantly passed through the solution during the reaction. The decomposition required about five hours for completion, and was cleaner than in the last experiment. Phenol and aldehyde were the only products that could be identified.

20 grams of the diazo compound was decomposed in ethyl alcohol, containing 20 per cent. of caustic potash. Decomposition took place at once, and was very rapid, being completed in about twenty minutes. A very large quantity of a tarry material was produced. Nothing but phenol could be identified, which was isolated as potassium phenolate.

20 grams of the diazo compound was decomposed in ethyl alcohol saturated with ammonia, and a stream of the gas, previously dried by passing over coarsely powdered quicklime, was conducted through the solution during the reaction. The flask in which the decomposition took place, was kept surrounded with ice-water. The decomposition commenced at once, and proceeded evenly, being completed in about two hours. No definite product other than phenol could be isolated. The odor of aldehyde was distinctly noticed, and its presence proved with a hot ammoniacal solution of silver nitrate.

20 grams of the diazo compound was decomposed with methyl alcohol, in the presence of ammonia, as in the last experiment. After the completion of the reaction, the alcohol was distilled off and the residue distilled with steam. The presence of phenol in both distillates was proved. The water distillate, on standing, changed color to bright green, and finally to an intense, beautiful blue, which changed to a bright red on the addition of an acid, and was restored when an excess of alkali was added. The color changes were very sharp and extremely delicate. An experiment made to determine the point, indicated that this color-reaction was due to a dye-stuff, formed by the oxidation in alkaline solution, of the product of the reaction of phenol on amidophenol. The presence of the amidophenol was probably due to some of it dissolving in the alcohol, without being acted upon by the nitrous acid in the diazotizing process. This coloring-matter

was probably present in very small quantities, as it was shown to have intense coloring-power.

20 grams of the diazo compound was decomposed in methyl alcohol saturated with hydrochloric acid, a stream of the dry gas being constantly passed through during the reaction. The decomposition was slow and regular, it being necessary to boil for about eight hours for completion. Phenol was the only product that could be identified.

There are several recorded cases of the decomposition of diazo compounds in the presence of sulphur dioxide. In this way Hübner,[1] in certain cases, was able to prepare the corresponding sulphonic acid. This suggested the following experiment:

40 grams of the diazo compound was decomposed in methyl alcohol saturated with sulphur dioxide, and a stream of the dried gas was passed through the solution during the decomposition, which required about eight hours at the boiling-point of the alcohol for completion. The alcohol was distilled off and shown to contain phenol. The residue was then carefully dried over the water-bath to insure the elimination of any hydrochloric acid, and then boiled with water and barium carbonate. It was then filtered and the filtrate examined for barium, but none was present. It is therefore improbable that a sulphonic acid was formed. No other definite product could be isolated.

It now seemed desirable to try the effect of sulphur dioxide in some neutral medium, which does not itself react with the diazo compound.

Therefore, 20 grams of the diazo compound was suspended in anhydrous ether, and a stream of sulphur dioxide passed in until the ether became saturated. Except a slight alteration in the color of the diazo compound, probably caused by the air brought in contact with it in the early part of the experiment, there was no evidence of any reaction taking place.

20 grams of the diazo compound was suspended in anhydrous ether, the whole surrounded with ice-water, and a stream of dry ammonia passed in. Decomposition commenced at once, and was quickly completed, the mass becom-

1 Ber. d. chem. Ges., 10, 1715.

ing black and tarry in appearance, but apparently containing some granular material. The ether was filtered off, the residue dried on bibulous paper, and examined. It apparently contained some amidophenol hydrochlorate, mixed with ammonium chloride, but it was not possible to separate them, and no definite statements can be made regarding the reaction.

Experiments were tried with the diazo compound and methyl alcohol, in which aniline or substituted anilines had been dissolved. In all these cases reaction took place at once, even in the cold, a gas being given off. Dilute acid was then added sufficient to dissolve out any unused aniline. The gummy residue was then filtered off, dried, and examined. No definite results, however, could be obtained.

Orthodiazophenol Chloride.—After a number of experiments I found that the best method, on the whole, for the preparation of the compound, was to make a thin paste of *o*-amidophenol hydrochlorate in alcohol, to keep this well cooled by a freezing-mixture, and to pass in rapidly a stream of nitrous acid, previously well cooled, until the whole mass was in solution, and the gas was no longer absorbed. The dark-colored solution resulting was then poured into a large quantity of well-cooled ether. The diazo salt soon separated out, but was generally slightly discolored greenish, which soon turned to brown on exposure to the air. A very pure specimen was obtained by dissolving in methyl alcohol at the room-temperature, and reprecipitating with strongly cooled ether. It soon became discolored on standing. Decomposed by heating on platinum foil, it gave off brownish fumes, and left a small residue of finely divided charcoal.

20 grams of the diazo compound was dissolved in ethyl alcohol, a marked diminution of temperature being noticed, and the solution becoming greenish in color. There was but little decomposition until the solution was warmed nearly to boiling, when it proceeded evenly and was completed in about three hours. Aldehyde was given off. The alcohol was distilled off and, on examination, was shown to contain phenol. The residue was now transferred to a distilling-bulb, and distilled, a mixture of alcohol and phenol distilling over until the

thermometer indicated 178°–180°, the boiling-point of phenol. After standing at this point for some time, it rapidly fell, a very small quantity of some crystalline material subliming from the residue at the same time. This sublimate could not be identified, and appeared to be a mixture.

20 grams of the diazo compound was dissolved in methyl alcohol, with marked lowering of the temperature. The decomposition was completed after boiling for about seven hours. The alcohol was distilled off and shown to contain phenol. The tarry residue was distilled, yielding phenol, but no other definite products.

50 grams of the diazo compound was decomposed in methyl alcohol saturated with hydrochloric acid, the decomposition being completed after boiling for about nine hours. The alcohol was distilled off and shown to contain phenol. The residue was distilled with steam, more phenol passed over, and a very small quantity of a yellow substance solidified in the condenser, which was shown by its melting-point and physical properties to be *o*-nitrophenol. Some of the original amido salt was then distilled with steam, and was found to contain a small quantity of unreduced *o*-nitrophenol.

40 grams of the diazo compound was then decomposed with methyl alcohol, in the presence of sulphur dioxide. The decomposition was completed after boiling for about nine hours. Attempts to detect the presence of a sulphonic acid were unavailing. Phenol was the only substance that could be identified.

Metadiazophenol Chloride.—The metamidophenol hydrochlorate was prepared as described by Ikuta,[1] with this modification, that it was crystallized from concentrated solutions by surrounding it with a freezing-mixture. After a number of attempts to prepare the diazo compound, and with very poor success, the following method was devised, and found to be quite satisfactory. The amido salt was dissolved in just sufficient 95 per cent. alcohol. A calculated amount of amyl nitrite was dissolved in about half the quantity of alcohol, and surrounded with a freezing-mixture of crushed ice and hydrochloric acid. Into this the solution of the amido salt was

[1] This JOURNAL, **15**, 39.

slowly poured, in very small quantities at a time, the whole being well stirred, and the temperature at no time allowed to rise to 0° C. After standing a few minutes, it was poured into a large amount of well-cooled ether. The diazo salt separated at once as a white crystalline precipitate, which soon changed color to red, and then brown. It was filtered rapidly with the aid of the pump, washed with dry ether, and dried as quickly as possible on a porous plate or bibulous paper, in as cool a place as was available. The freshly prepared compound was very unstable, exploding when struck or heated. 30 grams of the amido salt yielded 33 grams of the diazo salt.

A. Bantlin[1] treated a solution of metamidophenol in dilute sulphuric acid with potassium nitrite, and boiled with evolution of nitrogen. After cooling he extracted with ether, and obtained resorcinol from the extract. It seemed desirable to try the reaction with the diazo compound itself, however. Therefore, 30 grams of the diazo compound was dissolved in water and boiled. The decomposition was very rapid, a large amount of tarry material being formed. Extracted repeatedly with ether, and the extract evaporated, a dark-colored, disagreeable-looking residue was obtained, which, after standing several days, deposited white needles, but much discolored by a black tarry residue, from which it was impossible to separate them by crystallization. The yield was very small.

30 grams of the diazo compound was decomposed in water containing about 10 per cent. hydrochloric acid. The reaction appeared to be somewhat cleaner than in the last experiment. It was distilled with steam until the distillate no longer gave a precipitate with bromine water. Bromine water was now added until no further precipitate was obtained, the precipitate filtered off, recrystallized from alcohol, and identified by its melting-point as tribromresorcinol.

15 grams of the freshly prepared diazo compound was decomposed in ethyl alcohol. Decomposition commenced at once, and appeared to be complete in about an hour. It was then heated to boiling with apparently no further decomposition. The alcohol was distilled off and shown to contain phenol. Distilled with steam, more phenol came over and a tarry resi-

due was left in the flask. This residue was extracted with benzene and chloroform without success. It was then distilled, yielding a small quantity of phenol, and then charring.

30 grams of the diazo compound was decomposed with methyl alcohol. The decomposition commenced at once, and was completed in about an hour and a half. The alcohol was distilled off and the residue distilled with steam. Phenol was proved present in both distillates. No other product could be isolated.

Preparation of the Chlordiazobenzene and Bromdiazobenzene Salts.

The chlordiazobenzene salts, and the bromdiazobenzene salts used in this investigation, were all prepared in the same manner, and one description will apply to them all if the names of the particular anilines and acids be interpolated.

A weighed amount of the aniline was dissolved in a slight excess of the acid, and sufficient water added to make a thick paste, when surrounded with a freezing-mixture.

A rapid stream of nitrogen trioxide, prepared by decomposing strong nitric acid with arsenic trioxide, was passed through the paste, until the whole dissolved to a clear, dark-green solution, and the gas was no longer absorbed. The diazo salt was then precipitated by adding to a strongly cooled mixture of alcohol and ether. It was filtered off with the aid of the pump, washed with dry ether, and then dried on an unglazed plate and bibulous paper.

These salts were all white, crystalline substances, fairly stable in the air, and in no case here recorded was a discolored or suspicious specimen used.

The decompositions were carried on in suitable flasks fitted with return condensers, and arranged over wire gauze, as this was found to be most convenient for controlling the temperature during a reaction.

o-Chlordiazobenzene Nitrate.—20 grams *o*-chloraniline yielded 18 grams of the diazo salt.

15 grams of the diazo compound was added to about 150 cc. ethyl alcohol. It partially dissolved without decomposition. Warmed until decomposition had fairly commenced, the lamp

was withdrawn, and it proceeded spontaneously, evenly, and regularly, and appeared to be complete in about an hour and a half. It was then boiled for a half hour, to insure complete decomposition. Aldehyde was given off copiously during the reaction. Distilled with steam an oil passed over, which, separated and dried over calcium chloride, weighed 7.6 grams. It was distilled, boiling at 132°, and was identified as chlorbenzene. A small residue of tarry material was carefully examined, but from it nothing definite could be obtained.

15 grams of the diazo compound, with 150 cc. methyl alcohol, partially dissolved ; decomposition commenced at once, and proceeded slowly. After twenty-four hours it had ceased, but proceeded when the solution was warmed, and appeared to be complete after boiling for an hour. Distilled with steam, an oil separated, which was dried, weighed 7.5 grams, boiled at 131°–133°, and proved to be chlorbenzene, identical with that obtained in the last experiment. A small tarry residue was examined, without obtaining any other definite product.

o-Chlordiazobenzene Sulphate.—20 grams *o*-chloraniline yielded 24 grams of the diazo salt.

22 grams of the diazo compound dissolved in ethyl alcohol without decomposition. Warmed gently until decomposition had commenced it proceeded spontaneously, and developed so much heat that the flask and its contents had to be cooled by wiping it, from time to time, with a wet towel. The reaction was completed in about three-quarters of an hour, and it was then heated to boiling for half an hour. Aldehyde was given off during the reaction. Distilled with steam, an oil was separated, dried, and weighed 9 grams, and distilled over at 132°, showing the properties of chlorbenzene. No other definite product could be isolated.

25 grams of the diazo compound, with 200 cc. methyl alcohol, partially dissolved, decomposition beginning immediately, but proceeding very slowly. It was warmed from time to time, the decomposition being completed in about five hours. Distilled with steam an oil separated. It weighed 8.8 grams, distilled at 132°, and was identified as chlorbenzene. No other product could be isolated.

m-Chlordiazobenzene Nitrate.—20 grams *m*-chloraniline yielded 29.1 grams of the diazo salt.

25 grams of the diazo compound was decomposed with 200 cc. ethyl alcohol. Warming from time to time, the decomposition was completed in about three-quarters of an hour. Aldehyde was given off during the reaction. Distilled with steam an oil was separated, dried, weighed 9.1 grams, distilled at 132°–134°, and was identified as chlorbenzene. No other definite product could be isolated.

30 grams of the diazo compound, with 300 cc. methyl alcohol, partially dissolved with some decomposition, which had, however, not proceeded far after standing for sixty hours. It was then heated to boiling, and the decomposition was completed in an hour. On cooling, a voluminous, flocculent precipitate separated, which was filtered off and dried. It weighed 0.2–0.3 gram. It was but slightly soluble in alcohol or glacial acetic acid. The filtrate was distilled with steam, an oil separating, which was dried, weighed 12 grams, and distilled over, for the most part, at 187°–193°. A small residue of tarry material was examined, but yielded nothing definite.

m-Chlordiazobenzene Sulphate.—60 grams *m*-chloraniline yielded 110 grams of the diazo salt, a practically theoretical yield.

35 grams of the diazo compound, with 300 cc. ethyl alcohol, was warmed until decomposition had commenced, when it proceeded spontaneously, it being necessary to cool the flask by wiping it, from time to time, with a wet towel. The decomposition was completed in about an hour, aldehyde being given off during the reaction. Distilled with steam, an oil was separated, dried, weighed 15 grams, distilled over at 132°, and was identified as chlorbenzene. No other definite product could be isolated.

30 grams of the diazo compound, with 300 cc. methyl alcohol, partially dissolved and slowly decomposed. After standing sixty hours, it was necessary to boil for about two hours, to complete the decomposition. On cooling, a flocculent precipitate, apparently identical with the one obtained in the experiment described above, separated, was dried, and weighed

0.2 gram. The residue was distilled with steam, an oil was separated, dried, weighed 13 grams, and distilled, for the most part, at 187°–196°.

110 grams of the diazo compound, in two lots of 55 grams each, was decomposed with methyl alcohol, 300 cc. to each experiment. As in the last experiment, a flocculent precipitate separated after the decomposition was completed. It was filtered off, dried, and weighed 1.2 grams. The small quantity of this material, and its behavior toward solvents, prevented a further study of it. The filtrate was treated as in the last experiment, the greater portion of the oil distilling over at 187°-195°. No other definite products could be isolated. The three portions of oil, boiling above 186°, obtained from the decomposition of metachlordiazobenzene salts and methyl alcohol were now brought together, and subjected to fractional distillation. After four distillations, there was obtained a perfectly colorless, strongly refractive oil, possessing a peculiar, aromatic odor, and but faintly suggestive of anisol. It boiled constantly at 193°. It was analyzed for chlorine by the method of Carius.

Calculated for metachloranisol.	I.	Found.	II.
24.88	25.18		25.12

p-Chlordiazobenzene Nitrate.—30 grams *p*-chloraniline yielded 36 grams of the diazo salt.

35 grams of the diazo compound, with 300 cc. ethyl alcohol, partially dissolved without decomposing. Heated to boiling, the decomposition was completed in about two hours. The alcohol was distilled off, and an oil precipitated from the distillate by adding water. The residue was distilled with steam, an oil coming over at first, followed by some light yellow material, which solidified in the condenser. The two portions of oil were brought together and distilled, commencing to come over at 132°, but the thermometer slowly rising. The latter portion of the distillate had an odor strongly suggestive of phenetol. The oil was probably chlorbenzene, containing a small quantity of *p*-chlorphenetol, but the quantity of material at disposal was too small to permit of a good separation. The solid material was dissolved in caustic potash,

filtered, evaporated to a concentrated solution, reprecipitated with hydrochloric acid, dried, and weighed 2 grams. After several recrystallizations from alcohol, it melted constantly at 87°, and was identified as chlornitrophenol of the formula $C_6H_3\begin{cases} Cl & (1) \\ NO_2 & (3) \\ OH & (4) \end{cases}$. No other definite product could be obtained.

35 grams of the diazo compound, with 300 cc. methyl alcohol, partially dissolved without decomposition. After boiling for two hours the decomposition was completed. The alcohol was distilled off and an oil precipitated from it by adding water. The residue was distilled with steam, an oil coming over at first and then a solid material, as in the last experiment. The portions of oil (11 grams in all) were brought together, dried, and distilled, coming over at 200°. It was identified as *p*-chloranisol. The solid material was dried, and weighed 5.6 grams. This was dissolved in caustic potash, recrystallized, precipitated from a concentrated solution with hydrochloric acid, and recrystallized several times from alcohol, when it melted constantly at 87° and was identified as chlornitrophenol $C_6H_3\begin{cases} Cl & (1) \\ NO_2 & (3) \\ OH & (4) \end{cases}$. No other definite product could be isolated from the residue.

p-Chlordiazobenzene Sulphate.—30 grams *p*-chloraniline yielded 55 grams of the diazo salt, a practically theoretical yield.

20 grams of the diazo compound with 200 cc. ethyl alcohol partially dissolved without decomposition. On warming, the decomposition commenced and then proceeded spontaneously, it being necessary to cool the flask by wiping it from time to time with a wet towel. The decomposition was completed in about an hour, and it was then boiled for half an hour longer. Distilled with steam, 9 grams of an oil was separated, dried, and redistilled, boiling at 132°. It was identified as chlorbenzene. Further examination of the residue yielded nothing definite. It was carefully examined for the presence of a sulphonic acid, but none was found.

50 grams of the diazo compound with 350 cc. methyl alcohol, partially dissolved without decomposing. Decomposition was completed after boiling for about five hours. Distilled with steam an oil was separated, weighing 15.4 grams. This was dried and distilled at 200°. It was identified as *p*-chloranisol. No other product could be isolated from the residue.

o-Bromdiazobenzene Nitrate.—30 grams *o*-bromaniline yielded 38 grams of the diazo salt.

15 grams of the diazo compound with 150 cc. ethyl alcohol partially dissolved with slight decomposition. Warmed until the decomposition was started, it proceeded spontaneously, it being necessary to cool the flask from time to time. The decomposition was completed in three-quarters of an hour. It was then boiled for a quarter of an hour. Aldehyde was given off copiously. Distilled with steam, an oil weighing 8 grams was separated, dried, distilled at 153°–154°, and was identified as brombenzene. No other definite product could be identified.

30 grams of the diazo compound with 300 cc. methyl alcohol, partially dissolved with slight decomposition. After boiling two hours the decomposition was completed. The alcohol was distilled off, and from it an oil precipitated by the addition of water. Distilled with steam, the residue yielded more oil. The two portions were brought together and dried. They weighed 12 grams. The oil distilled over at 153°-156°, and was then identified as brombenzene. No other definite product could be isolated.

o-Bromdiazobenzene Sulphate.—20 grams *o*-bromaniline yielded 31 grams of the diazo salt.

25 grams of the diazo compound with 250 cc. ethyl alcohol, partially dissolved without decomposition, even after standing several hours. Warmed until decomposition commenced, it proceeded spontaneously, the flask being cooled, from time to time, with a wet towel, to prevent too vigorous a reaction. The decomposition appeared to be complete in about a half hour. It was then boiled for a quarter of an hour longer. Distilled with steam, an oil was separated and dried. It weighed 10 grams, distilled at 154°, and was identified as brombenzene.

30 grams of the diazo compound, with 250 cc. methyl alcohol, partially dissolved, with slight decomposition, after standing an hour. It was then heated to boiling for five hours, when the decomposition was completed. Distilled with steam, an oil weighing 13 grams was separated and dried. It distilled at 154°, and was identified as brombenzene. A further examination of the residue yielded nothing definite.

m-Bromdiazobenzene Nitrate.—30 grams *m*-bromaniline yielded 34 grams of the diazo salt.

25 grams of the diazo compound, with 250 cc. ethyl alcohol, partially dissolved, with slight decomposition, after standing about 20 hours. Warmed until decomposition commenced, it proceeded spontaneously, and was completed in about three-quarters of an hour. It was then boiled for half an hour. Aldehyde was given off during the reaction. Distilled with steam an oil was obtained that weighed 11 grams and distilled over at 153°–156°. It was redistilled and identified as brombenzene. No other definite product could be isolated.

30 grams of the diazo compound with 250 cc. methyl alcohol, partially dissolved, with slight decomposition, after standing about twelve hours. Heated to boiling, the decomposition appeared to be complete in about an hour, and the boiling was continued for a half hour longer. On cooling, a voluminous flocculent precipitate separated which weighed 12 grams. On redistilling this oil the thermometer rose rapidly to 206°, and then slowly to 217°, by far the greater portion coming over between these figures (see next page). Further examination of the residue yielded nothing definite.

m-Bromdiazobenzene Sulphate.—30 grams *m*-bromaniline yielded 33 grams of the diazo salt.

25 grams of the diazo compound with 250 cc. ethyl alcohol, partially dissolved, with very slight decomposition, after standing twenty hours. Warmed until decomposition commenced, it proceeded spontaneously, and was completed in about an hour. It was then boiled for a half hour. Aldehyde was given off copiously. Distilled with steam an oil weighing 9 grams was obtained. It distilled entirely at 154°,

and was identified as brombenzene. No other product could be isolated.

30 grams of the diazo compound with 250 cc. methyl alcohol, partially dissolved, with slight decomposition, after standing twelve hours. Heated to boiling, the decomposition appeared to be complete in about an hour, but the boiling was continued for a half hour longer. On cooling, a voluminous, flocculent precipitate separated, which, when dried, weighed 0.15 gram. The filtrate was distilled with steam, when an oil weighing 11 grams separated. This was redistilled when about three-quarters of it came over at 207°–216°.

60 grams of the diazo compound with 300 cc. methyl alcohol, was decomposed, as in the last experiment. After cooling, the flocculent precipitate was filtered off, dried, and weighed 0.4 gram. It was brought together with the portion obtained in the last experiment, and unsuccessful attempts were made to crystallize it. The quantity of this material at disposal, and its conduct toward solvents, made a further study of it impossible.

The filtrate distilled with steam, yielded 20.5 grams of oil, which, for the most part, distilled over at 206°–217°. This portion was again distilled, yielding 15.5 grams of a colorless oil, strongly refracting, and with an odor strongly suggestive of the *m*-chloranisol, before described. It was analyzed for bromine by the method of Carius.

Calculated for *m*-bromanisol.	I.	Found. II.
42.7	44.6	44.5

The oil was again fractioned twice, and a portion, about 8 grams, was obtained, which distilled constantly at 214°, and was analyzed.

Calculated.	I.	Found. II.
42.7	43.5	43.6

It seemed probable that the substance was *m*-bromanisol, containing some brombenzene in solution, which could not be completely separated with the quantities at disposal. The residue was examined, but nothing definite obtained.

p-Bromdiazobenzene Nitrate.—40 grams *p*-bromaniline yielded 46 grams of the diazo salt.

55 grams of the diazo compound with 400 cc. ethyl alcohol, was boiled for about four hours, when the decomposition was completed. Aldehyde was copiously evolved. The alcohol was distilled off, and from it an oil separated on the addition of water. The residue was distilled with steam, an oil separating in the distillate. The two portions of oil were brought together, dried, and weighed 24 grams. It distilled at 154°, and was identified as brombenzene. No other definite product could be isolated.

20 grams of the diazo compound with 200 cc. methyl alcohol, partially dissolved, without decomposition. On gently warming, the decomposition proceeded evenly and was completed in about one and one-half hours. It was then boiled for twenty minutes. The alcohol was distilled off, and from it an oil precipitated by adding water. The residue was distilled with steam, an oil coming over at first and then a yellow, solid material. The portions of oil were brought together, dried, weighed 12 grams, and distilled at 220°–222°, being identified as *p*-bromanisol. The solid material was dissolved in caustic potash, recrystallized, and precipitated with hydrochloric acid. It weighed 1.5 grams. After crystallizing from alcohol it melted sharply at 88° and was identified as bromnitrophenol of the formula $C_6H_3 \begin{cases} Br & (1) \\ NO_2 & (3) \\ OH & (4) \end{cases}$. No other definite product could be isolated.

p-Bromdiazobenzene Sulphate.—30 grams *p*-bromaniline yielded 39 grams of the diazo salt.

20 grams of the diazo compound with 200 cc. ethyl alcohol, was warmed until decomposition commenced, when it proceeded spontaneously, it being necessary to cool the flask, from time to time with a wet towel. The decomposition appeared to be complete in about three-quarters of an hour, and it was then boiled for twenty minutes longer. Aldehyde was evolved copiously. Distilled with steam 9 grams of an oil was obtained that distilled at 154°, and was identified as brombenzene. No other product could be isolated.

35 grams of the diazo compound with 300 cc. methyl alcohol, partially dissolved without decomposition. After boiling five hours the decomposition was completed. Distilled with steam, an oil was separated, dried, and weighed 14 grams. It distilled at 220°–223°, and was identified as *p*-bromanisol. No other definite product could be isolated.

<div align="center">SUMMARY.</div>

<div align="center">*The Diazophenols.*</div>

The experiments with the diazophenols here recorded are to be regarded as indecisive, as to the main object of this research. The only reactions that could be followed are expressed by these equations :

$$C_6H_4\begin{cases}OH \\ N_2Cl\end{cases} + HOH = C_6H_4\begin{cases}OH \\ OH\end{cases} + N_2 + HCl.$$

$$C_6H_4\begin{cases}OH \\ N_2.Cl\end{cases} + CH_3OH = C_6H_5.OH + N_2 + H.CHO + HCl.$$

$$C_6H_4\begin{cases}OH \\ N_2.Cl\end{cases} + C_2H_5OH = C_6H_5.OH + N_2 + CH_3.CHO + HCl.$$
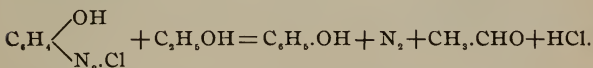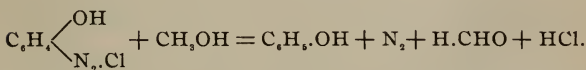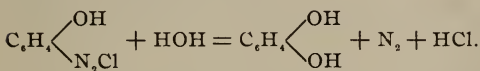
Or, in other words, the "oxy" reaction takes place, when a diazophenol is decomposed with water, and the hydrogen reaction with methyl or ethyl alcohol.

It does not seem probable that the alkoxy reaction took place to any extent, in any of the experiments described, because the products that would have been formed could have been readily recognized from their recorded properties.

But it became evident in the course of the work on these substances that they are extremely unstable, very sensitive toward reagents, reacting themselves with the products of decomposition, so that secondary complicated reactions took place to such a degree as to modify and mask the expected reactions, if indeed, they took place at all. The main results are summarized below, and these results compared with others previously obtained.

The Chlordiazobenzenes.

Orthochlordiazobenzene salts with ethyl alcohol, as far as could be determined, gave the hydrogen reaction alone, as expressed by these equations :
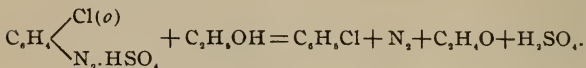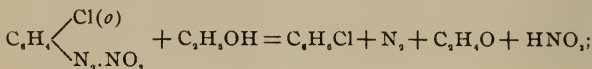
$$C_6H_4{<}^{Cl(o)}_{N_2.NO_3} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + HNO_3;$$

$$C_6H_4{<}^{Cl(o)}_{N_2.HSO_4} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4.$$

Orthochlordiazobenzene salts with methyl alcohol gave the hydrogen reaction alone :

$$C_6H_4{<}^{Cl(o)}_{N_2.NO_3} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + HNO_3;$$

$$C_6H_4{<}^{Cl(o)}_{N_2.HSO_4} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + H_2SO_4.$$

Metachlordiazobenzene salts with ethyl alcohol gave the hydrogen reaction only.

$$C_6H_4{<}^{Cl(m)}_{N_2.NO_3} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + HNO_3;$$

$$C_6H_4{<}^{Cl(m)}_{N_2.HSO_4} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4.$$
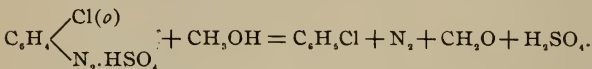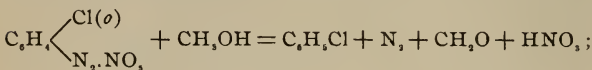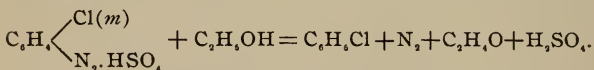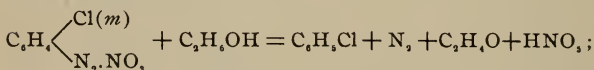
Metachlordiazobenzene salts with methyl alcohol gave more complicated reactions. The methoxy reaction apparently predominated, metachloranisol being the principal product :

$$C_6H_4{<}^{Cl(m)}_{N_2.NO_3} + CH_3OH = C_6H_4{<}^{Cl(m)}_{OCH_3} + N_2 + HNO_3;$$

$$C_6H_4{<}^{Cl(m)}_{N_2.HSO_4} + CH_3OH = C_6H_4{<}^{Cl(m)}_{OCH_3} + N_2 + H_2SO_4.$$
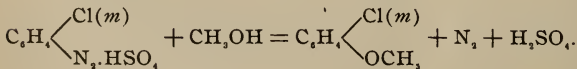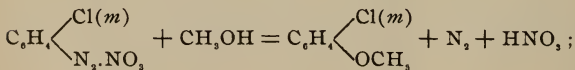
At the same time it appeared that the hydrogen reaction took place to a slight extent :

$$C_6H_4\Big\langle {}^{Cl(m)}_{N_2.NO_3} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + HNO_3;$$

$$C_6H_4\Big\langle {}^{Cl(m)}_{N_2.HSO_4} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + H_2SO_4.$$
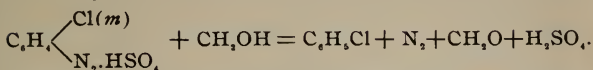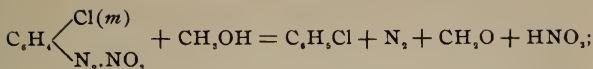
A small quantity of a well characterized solid was also formed, the nature of which was not determined.

Parachlordiazobenzene nitrate and ethyl alcohol gave principally the hydrogen reaction as expressed thus:

$$C_6H_4\Big\langle {}^{Cl(p)}_{N_2.NO_3} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + HNO_3.$$
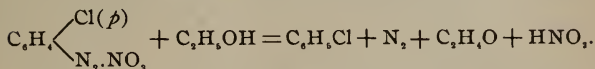
But at the same time, to no inconsiderable extent, the ethoxy reaction:

$$C_6H_4\Big\langle {}^{Cl(p)}_{N_2.NO_2} + C_2H_5.OH = C_6H_4\Big\langle {}^{Cl(p)}_{OC_2H_5} + N_2 + HNO_3,$$
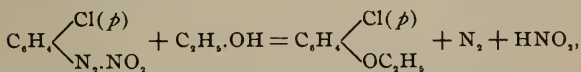
accompanied by the formation of chlornitrophenol $C_6H_3\begin{cases} Cl & (1) \\ NO_2 & (3) \\ OH & (4) \end{cases}$. The formation of a nitrophenol seems to be strictly analogous to the cases already carefully studied by Remsen and Orndorff,[1] of the action of diazobenzene nitrate on ethyl alcohol, and by Beeson[2] of the action of the diazo compound on methyl alcohol. From careful work on this point, these investigators concluded that the substance was formed by the elimination of nitrogen, and a molecular rearrangement of the diazo salt. Work done by Chamberlin[3] in this laboratory makes it appear probable that the alkoxy product is first formed, that this is then nitrated to some extent by the acid liberated in the reaction, and finally that the nitroether thus formed is saponified by boiling with the dilute acid, as in the formation of nitrocresols, from the nitration of cresol ethers, studied by Staedel.[4] I regret that circumstances prevented me from studying the nitration of chlorophenol ethers in this connection.
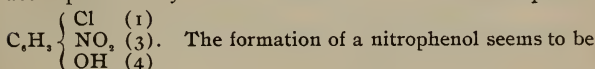
[1] This JOURNAL, **9**, 389   [2] *Ibid*, **16**, 235.
[3] *Ibid*, **19**, 531.   [4] Ann. Chem. (Liebig), **217**, 158.

Parachlordiazobenzene sulphate and ethyl alcohol, as far as could be determined, gave only the hydrogen reaction :

$$C_6H_4 \begin{matrix} Cl(p) \\ N_2.HSO_4 \end{matrix} + C_2H_6OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4.$$
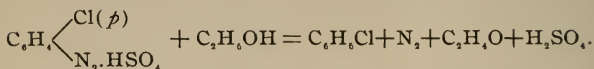
These last two experiments suggest, in a marked manner, what has been indicated by other work,[1] that the acid residue forming the salt of the diazo compound influences, to some degree, the nature of the reaction.

Parachlordiazobenzene nitrate and methyl alcohol gave the methoxy reaction entirely :

$$C_6H_4 \begin{matrix} Cl(p) \\ N_2.NO_3 \end{matrix} + CH_3.OH = C_6H_4 \begin{matrix} Cl(p) \\ OCH_3 \end{matrix} + N_2 + HNO_3.$$
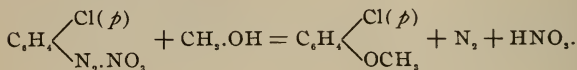
At the same time some chlornitrophenol was formed,
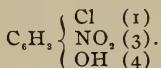
$$C_6H_3 \begin{cases} Cl & (1) \\ NO_2 & (3) \\ OH & (4) \end{cases}.$$

Parachlordiazobenzene sulphate with methyl alcohol gave the methoxy reaction alone :

$$C_6H_4 \begin{matrix} Cl(p) \\ N_2.HSO_4 \end{matrix} + CH_3OH = C_6H_4 \begin{matrix} Cl(p) \\ OCH_3 \end{matrix} + N_2 + H_2SO_4.$$
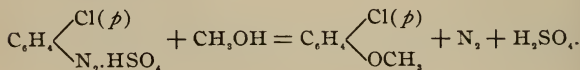
The Bromdiazobenzenes.

Orthobromdiazobenzene salts with ethyl alcohol gave only the hydrogen reaction :

$$C_6H_4 \begin{matrix} Br(o) \\ N_2.NO_3 \end{matrix} + C_2H_6OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3;$$

$$C_6H_4 \begin{matrix} Br(o) \\ N_2.HSO_4 \end{matrix} + C_2H_6OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4.$$
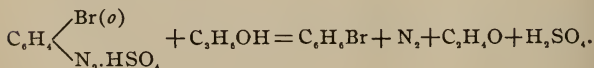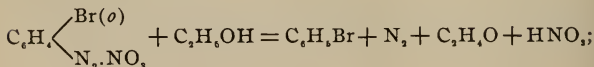
Orthobromdiazobenzene salts with methyl alcohol gave only the hydrogen reaction :

[1] Remsen and Graham : This JOURNAL, **11**, 330.
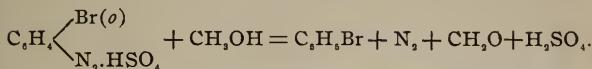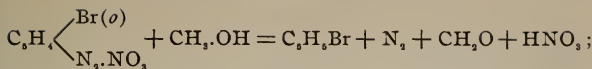
$$C_6H_4\big<^{Br(o)}_{N_2.NO_3} + CH_3.OH = C_6H_5Br + N_2 + CH_2O + HNO_3 ;$$

$$C_6H_4\big<^{Br(o)}_{N_2.HSO_4} + CH_3OH = C_6H_5Br + N_2 + CH_2O + H_2SO_4.$$

Metabromdiazobenzene salts with ethyl alcohol gave only the hydrogen reaction :

$$C_6H_4\big<^{Br(m)}_{N_2.NO_3} + C_2H_6OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3 ;$$

$$C_6H_4\big<^{Br(m)}_{N_2.HSO_4} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4.$$
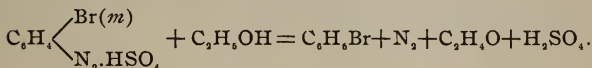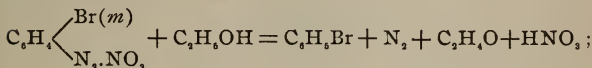
Metabromdiazobenzene salts with methyl alcohol gave principally the methoxy reaction :

$$C_6H_5\big<^{Br(m)}_{N_2.NO_3} + CH_3OH = C_6H_4\big<^{Br(m)}_{OCH_3} + N_2 + HNO_3,$$

$$C_6H_4\big<^{Br(m)}_{N_2.HSO_4} + CH_3OH = C_6H_4\big<^{Br(m)}_{OCH_3} + N_2 + H_2SO_4;$$
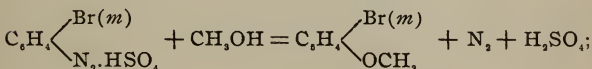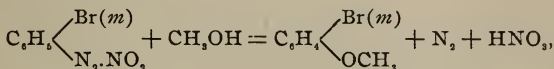
and at the same time to an undetermined, but probably small extent, the hydrogen reaction took place :

$$C_6H_5\big<^{Br(m)}_{N_2.NO_3} + CH_3OH = C_6H_5Br + N_2 + CH_2O + HNO_3 ;$$

$$C_6H_4\big<^{Br(m)}_{N_2.HSO_4} + CH_3OH = C_6H_5Br + N_2 + CH_2O + H_2SO_4.$$
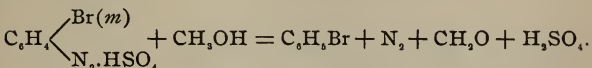
Parabromdiazobenzene salts with ethyl alcohol yielded only the hydrogen reaction :

$$C_6H_4\big<^{Br(p)}_{N_2.NO_3} + C_2H_6OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3 ;$$

$$C_6H_4\big<^{Br(p)}_{N_2.HSO_4} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4.$$
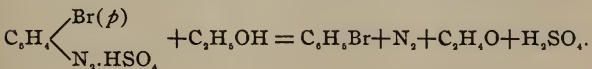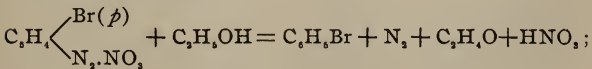
Parabromdiazobenzene nitrate with methyl alcohol gave the methoxy reaction:

$$C_6H_4 {<}^{Br(p)}_{N_2.NO_3} + CH_3OH = C_6H_4 {<}^{Br(p)}_{OCH_3} + N_2 + HNO_3,$$
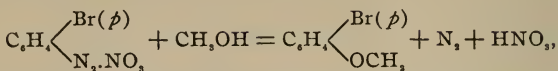
and at the same time was formed some bromnitrophenol,

$$C_6H_3 \begin{cases} Br & (1) \\ NO_2 & (3) \\ OH & (4) \end{cases}$$
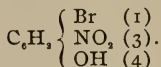
Parabromdiazobenzene sulphate with methyl alcohol yielded the methoxy reaction alone:

$$C_6H_4 {<}^{Br(p)}_{N_2.HSO_4} + CH_3OH = C_6H_4 {<}^{Br(p)}_{OCH_3} + N_2 + H_2SO_4.$$
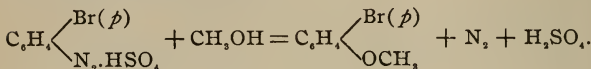
CONCLUSIONS.

There are now, excluding the diazophenols, five cases available for comparison, and the discussion of the primary objects of this investigation, the decomposition with water, methyl and ethyl alcohol, of diazobenzene, diazobenzoic acids, chlordiazobenzenes, bromdiazobenzenes, and the nitrodiazobenzenes.

It has seemed to me better, on the whole, to discuss these cases together, and to facilitate this, I have tabulated the results of the experiments with methyl and with ethyl alcohol. There is no reason to believe that in any of these cases, the reaction with water would be otherwise than normal, so that the reaction with it need not be included.

With Methyl Alcohol.

	Ortho.	Meta.	Para.
Diazobenzene		Methoxy entirely	
Diazobenzoic acid	Methoxy	Methoxy	Methoxy
Chlordiazobenzene	Hydrogen	Methoxy in excess of hydrogen.	Methoxy
Bromdiazobenzene	Hydrogen	Methoxy in excess of hydrogen.	Methoxy
Nitrodiazobenzene	Hydrogen	Hydrogen and methoxy in traces.	Hydrogen and methoxy 8%.

With Ethyl Alcohol.

	Ortho.	Meta.	Para.
Diazobenzene		Ethoxy in excess of hydrogen	
Diazobenzoic acid	Hydrogen	Hydrogen *in excess of ethoxy.*	Ethoxy
Chlordiazobenzene	Hydrogen	Hydrogen	Hydrogen *in excess of ethoxy.*
Bromdiazobenzene	Hydrogen	Hydrogen	Hydrogen
Nitrodiazobenzene	Hydrogen	Hydrogen	Hydrogen

A study of all the facts indicated by these tables seems to me to warrant the following conclusions :

1. The alkoxy reaction is normal, and the hydrogen reaction, when it takes place, is a modification induced by special conditions.

2. Regarding water as the first member of the series, the more complex the alcohol, the greater the tendency towards the hydrogen reaction. This is in accordance with the view expressed by Metcalf.[1]

3. That acid radicals, as COOH, Cl, Br, NO_2, etc., induce the hydrogen reaction, and their influence in this respect is probably in the order in which they are here named. This is in accordance with the views expressed by Remsen and Graham,[2] from a study of all the cases on record in which these radicals occur.

4. That the presence of the substituting radical in the ortho position is most favorable to the hydrogen reaction, and the meta position more favorable than the para.

REVIEWS.

LABORATORY EXPERIMENTS ON THE CLASS REACTIONS OF ORGANIC SUBSTANCES AND THEIR IDENTIFICATION. By ARTHUR A. NOYES, PH.D., Assistant Professor of Organic Chemistry in the Massachusetts Institute of Technology, and SAMUEL P. MULLIKEN, PH.D., Instructor of Organic Chemistry in the Massachusetts Institute of Technology. Easton, Pa.: Chemical Publishing Co. 1897. 28 pp. Price 50 cents.

The object of this book is clearly stated in the title. To quote from the preface of the authors : "Experience has shown that the preparation of typical organic substances in accordance with the plans followed in the manual of Gattermann, Levy, Fischer, etc., teaches satisfactorily the manipulative methods of organic chemistry and the manner of execu-

[1] This JOURNAL, **15**, 301.   [2] *Ibid*, **11**, 331.

tion of the leading synthetic processes, but that it fails to a surprising extent in the case of most students to give a knowledge of the important characteristics of the various classes of organic compounds, and therefore of the fundamental principles of the science. Unless an instructor is continually on the alert, the course of preparation work becomes almost inevitably a routine following the direction.'' The last sentence must go straight to the heart of every teacher who has tried to deal conscientiously with his students. That dreadful tendency to get in a rut, to work mechanically, to let the fingers move without any accompanying action of the mind, is known to us all. The only way in which it can possibly be mitigated—it cannot be prevented entirely—is to have an instructor ''continually on the alert.'' No scheme, written, or printed, or spoken, can do anything like as much as the living teacher at the elbow of the worker.

There are, however, books that drive one into a routine at once, and others that do not, and any book of the latter character must be helpful in a laboratory. This little work of Messrs. Noyes and Mulliken belongs to the second class and will be of service. It is made up of three parts.

Part I deals with experiments illustrating the class reactions of organic compounds; detection of water in organic compounds; the reactions distinguishing double and triple-bonded from single-bonded compounds; the reactions of triple-bonded compounds; the behavior of hydrocarbons in general; the reactions of compounds containing the hydroxyl group; the reactions of alcohols and phenols; the reactions of organic acids; the reactions of aldehydes, etc.

Part II deals with experiments illustrating the methods of detection of nitrogen, sulphur, and halogens in organic compounds; and Part III with the identification and separation of unknown organic substances.   I. R.

PRACTICAL EXERCISES IN ELECTROCHEMISTRY. By DR. FELIX OETTEL. Translated (with the author's sanction) by EDGAR F. SMITH, Professor of Chemistry in the University of Pennsylvania. Philadelphia, Pa.: P. Blakiston, Son & Co. 1897. 92 pp.

This little book is intended to furnish chemical students with directions for a brief course of experiments in the application of electrochemical methods to chemistry. The first part deals with the sources of current, regulators, measuring apparatus, and methods of dealing with the current in general. Among the experiments illustrating the application of electrical methods to chemical reactions are the formation of hypochlorites and chlorates; the electrolysis of hydrochloric acid without a diaphragm; the electrolysis of sulphuric acid;

the electrolysis of a salt solution with use of a diaphragm; the use of hydrochloric acid with a diaphragm ; the formation of persulphuric acid by electrolysis of sulphuric acid ; the preparation of magnesium ; the electrolysis of fused lead chlorate; the electrolysis of sodium acetate ; the reduction of nitrobenzene to azobenzene, etc.

An advanced student in chemistry who has the time at his disposal would do well to perform a number of these experiments. This branch of chemistry is coming more and more into prominence, and it is well to get at least a glimpse of the methods that are in use. It may fairly be assumed that the methods described are well described and that the translation is well done. I. R.

TEXT-BOOK OF PHYSICAL CHEMISTRY. By CLARENCE L. SPEYERS, Associate Professor of Chemistry, Rutgers College. New York : D. Van Nostrand Company. pp. 224. 1897.

The subject is treated primarily from the standpoint of energy. In his preface the author says : '' I have adopted the view that matter is a collection of energies in space, considering the relations of the energies to be the prime object of investigation. With Ostwald, I feel confident that the materialistic interpretation has passed its prime, and has no promise for the future.''

The various manifestations of energy are taken up first, while volume energy is dealt with more fully in the chapter on gases. The fundamental laws of thermodynamics are discussed under the heading, Heat. Various properties of solutions, such as Osmotic Pressure, Vapor Pressure, etc., are considered under the title, Physical Changes. In this same part of the book, the work on Molecular Weight of Liquids is also taken up. In the chapter on Equilibrium we find a mathematical discussion of the Conditions of Equilibrium, Equilibrium in Gaseous, Liquid, and Solid Systems, also in Solid-gas, Liquid-gas, and Solid-liquid Systems. A brief treatment of Chemical Kinetics gives the equations for what are termed monad, diad, and triad reactions, and the chapter on Phases, treats of the Conditions of Equilibrium, Monad, and Diad Systems.

The last fourth of the book is devoted to the important and interesting subject of Electrochemistry, including the Laws of the Current, the Ionic Condition in Solution, the Conductivity of Solutions, the Migration Velocity of the Ions, the Source of the Potential in Primary Cells, the Gas Battery, Polarization, Constant Cells, etc., and a few pages are devoted to Electrolytic Separations, and Electrochemical Analysis.

The book concludes with a very brief account of the general properties of ions, and the modes of their formation.

H. C. J.

MANUEL D' ANALYSE CHIMIQUE APPLIQUÉE À L' EXAMEN DES PRODUITS INDUSTRIELS ET COMMERCIAUX. Par Émile Fleurent. Paris: Georges Carré et C. Naud. 1898. pp.582.

This work proposes to give, chiefly for the use of those practically concerned with chemical industry, a condensed account of the general methods of inorganic analysis—qualitative and quantitative—and of elementary organic analysis, and a selection of special methods (in most cases but one of each kind—it would have been well to add at least references to others) for the examination of the principal raw materials and products which the chemist is called upon to investigate.

It may be feared that in the first or general part the aim of the author, to condense a large subject into as small a space as possible, has rendered the book of little use to a beginner, or to anyone trusting to this as his only guide—many important details, precautions, and references to possible complications being omitted—while the very general directions given are needless in the case of one who has already practically studied the subject with the aid of one of the more extended treatises.

The same remarks may be made in regard to the inorganic division of the special part of the work. For example, about two pages only are given to the determination of silver in its ores, including cupellation ; fuel is disposed of in less than two pages ; and about three and a half pages are devoted to the analysis of wrought and cast iron and steel. There are brief but sensible suggestions as to the taking of samples, a matter often less carefully considered than its real importance demands.

Some of the subjects in the organic division of the special part are treated of in much more detail, and are likely to be of much more use to practical workers in the laboratory. This is true of the chapters on fats and oils (methods in use in the *Laboratoire Municipal de Paris*) on butter and its adulterants (method of Müntz), on beet-sugar, its by-products and related materials, on grapes and other fresh fruits (method of Aimé Girard and Lindet), on wine, distilled spirits (notice of the estimation of furfural), determination of acetone in crude wood-spirit and '' denaturalized'' alcohols, etc. The methods given are for the most part those of French chemists, and in some instances deserving of special attention ; in other cases valuable processes which have been

worked out elsewhere, are unduly neglected and passed over
without notice.

Some important subjects are altogether omitted, for in-
stance the chemical examination of explosives. The print-
ing is clear and good, and there are neat illustrative engra-
vings. There is a table of contents, but no alphabetic index,
as is so often the case with books published in France.

J. W. M.

THE PRINCIPLES OF CHEMISTRY. By D. MENDELÉEF. Translated
from the Russian (sixth edition) by GEORGE KAMENSKY, A.R.S.M.,
of the Imperial Mint, St. Petersburg, Member of the Russian
Physico-Chemical Society. Edited by T. A. LAWSON, B.Sc., Ph.D.,
Examiner in Coal-tar Products to the City and Guilds of London In-
stitute, Fellow of the Institute of Chemistry. In Two Volumes.
Longmans, Green & Co., 39 Paternoster Row, London, New York,
and Bombay. 1897. Vol. I., 621 + xviii pp. Vol. II., 518 pp. 8vo.
Price $10.00.

When the first German edition of this book appeared in
1891, a review of it was published in this Journal (Vol. 13,
p. 139), which closed with the following words: "Every
teacher and every advanced student of chemistry should read
and study this book with care. Even the most experienced
teacher will find much in it that will prove of value to him."

At the present time, the book is so well known that a review
of this new edition may be regarded as superfluous. Of course
the new is better than the old edition. It has been carefully
brought up to date. Argon and helium, hydrazine and hy-
dronitrous (triazoic) acid, the nitrides and carbides which
Moissan has brought into such prominence during the last
few years, all of these are treated of—some very fully, others
meagerly. It matters little, however, whether one or
another compound may have been overlooked, the book is
not intended for reference, but for study, and to this it is ad-
mirably suited, not certainly on account of its orderliness, for
there are few books on chemistry less orderly, but on account
of the spirit that breathes through it, and that stimulates the
student, young or old. It is thoughtful, and therefore helpful.
The author has his own ideas on all subjects, and he seems
to be at the side of the reader with some valuable sugges-
tion, no matter how apparently trivial the particular subject
may be which is under treatment.

In regard to the original sixth edition, of which the book
before us is a translation, the author says: In this the sixth
edition I have not altered any essential features of the original
work, and have retained those alterations which were intro-
duced into the fifth edition. I have, however, added many
newly-discovered facts, and in this respect it is necessary to

say a few words.   Although all aspects of the simplest chemical relations are as far as possible equally developed in this book, yet on looking back I see that I have, nevertheless, given most attention to the so-called indefinite compounds, examples of which may be seen in solutions.   I recur repeatedly to them, and to all the latest data respecting them, for in them I see a starting-point for the future progress of our science, and to them I affiliate numerous instances of indefinite compounds, beginning with alloys and silicates, and ending with complex acids.   *   *   *   My own view is that a solution is a homogeneous liquid system of unstable dissociating compounds of the solvent with the substance dissolved.   *   * At present, my ideas respecting solutions are shared by few, but I trust that by degrees the instances I give will pave the way for their general recognition.''   I. R.

CORRESPONDENCE.

WASHINGTON, D. C., FEBRUARY 14, 1898.

Editor of the American Chemical Journal :

Dear Sir.—The Organization Committee of the Third International Congress of Applied Chemistry which is to be held in Vienna during the coming summer, has fixed the date of the meeting from July 28, to August 2, 1898.   Some time during the month of February, programs and announcements will be sent to all persons who have been enrolled as members of the Congress.

Respectfully,

H. W. WILEY,
Chairman of the American Committee.

AMERICAN

CHEMICAL JOURNAL

AN INVESTIGATION OF SOME DERIVATIVES OF ORTHOSULPHOBENZOIC ANHYDRIDE.[1]

By Michael Druck Sohon.

The investigations in this laboratory of the derivatives of orthosulphobenzoic acid, formed from the two isomeric chlorides of this acid, have shown many analogies and not less striking differences to the behavior of phthalic acid derivatives under similar conditions. It became, therefore, of interest to ascertain how the anhydride of orthosulphobenzoic acid would conduct itself toward reagents. To investigate this the present work was undertaken at the suggestion of Professor Remsen.

The anhydride of orthosulphobenzoic acid was prepared by Fahlberg and Barge,[2] by the action of acetyl chloride on the free acid ; also by action of phosphorus pentachloride on the neutral potassium salt, the reaction being effected in a sealed tube, at 170°. They describe it as monoclinic crystals, melting at 119°.

About the same time Remsen and Dohme[3] obtained it by heating a mixture of the acid and phosphorus pentoxide at

130°, as a sublimate consisting of fine needles, melting at 128°.

Oscar Weber,[1] by the action of acetyl chloride, on meta-sulphoparatoluic acid, derived from "methyl saccharin," obtained its anhydride, and studied the action of ammonia upon it.

The anhydrides of various nitrosulphobenzoic acids have been obtained by workers in this laboratory.

The material used for the preparation of the anhydride in this work was the acid potassium salt of orthosulphobenzoic acid, obtained from commercial "saccharin" (containing about 60 per cent. benzoic sulphinide) by substantially the same method as described by Remsen and Saunders.[2]

The difficulties of handling and preserving the solutions in anhydrous ether or benzene led to the rejection of the methods of Fahlberg and Barge and of Weber. Sublimation did not yield the anhydride in sufficient quantity; moreover the crystals thus obtained, fine needles, decomposed much more rapidly than the large crystals obtained by the following

Method of Preparation.

The well-dried and powdered acid potassium salt (about 25 grams) is intimately mixed in a mortar, with the equivalent amount of phosphorus pentachloride (22 grams). The temperature at which the action begins varies with the purity of the chemicals. With pure, dry reagents it is difficult to induce action, but the presence of a small amount of phosphorus oxychloride considerably lowers the required temperature. After the evolution of hydrochloric acid has ceased, the mass is heated for some time to expel some of the oxychloride, and to melt the product which is then disintegrated on cooling, and placed in a continuous extractor and the separation effected by benzene. The supersaturated benzene solution in the extractor is allowed to cool very slowly and clear, colorless crystals, often 10 to 15 mm. in their longer diameter, and practically pure, are deposited.

The benzene employed must be pure; otherwise dark, sometimes blue, tarry products are obtained (an ethereal solution

[1] Ber. d. chem. Ges., **22**, 1739.   [2] This JOURNAL, **17**, 347.

of the anhydride with some thiophene deposited a blue mass on exposure to the light). The presence of the phosphorus oxychloride in the solvent seems to favor the formation of better crystals.

A simple and efficient extractor was prepared from ordinary laboratory apparatus. A test-tube 200 × 25 mm. was perforated with 20 or 30 holes, made by plunging a heated platinum wire through the glass. The mouth was then contracted to about 15 mm. in diameter, and several larger openings made near this end. In this the material to be extracted was placed, suspended by a platinum wire in a long-necked balloon-flask connected with an inverted condenser, and immersed in a water-bath, the single connection between flask and condenser being effected by means of a rubber stopper. The upper end of the condenser was provided with a calcium-chloride tube.

The reaction between the salt and pentachloride may be expressed:

$$C_6H_4{\diagup {}^{COOH}_{\diagdown SO_2OK}} + PCl_5 = C_6H_4{\diagup {}^{CO}_{\diagdown SO_2}}\!\!\diagdown O + KCl + HCl +$$
$$POCl_3.$$
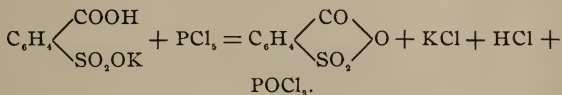
Limpricht and Uslar[1] have described a monochloride of metasulphobenzoic acid. It was thought that such a compound might be formed with the ortho acid, and break down with the formation of the anhydride, thus:

$$C_6H_4{\diagup {}^{COOH}_{\diagdown SO_2OK}} \longrightarrow C_6H_4{\diagup {}^{COOH}_{\diagdown SO_2Cl}} \longrightarrow C_6H_4{\diagup {}^{CO}_{\diagdown SO_2}}\!\!\diagdown O + HCl.$$
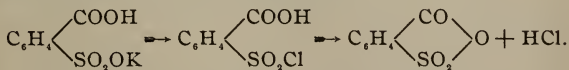
The reaction with pentachloride was brought about at a low temperature and the resulting mass poured into cold water. A bulky, flocculent precipitate separated which was washed with water until free from hydrochloric acid, and then dried between filter-paper. It seemed to have a definite melting-point and gave off hydrochloric acid when heated, and the residue was the anhydride. But, as the action of the pentachloride in sufficient proportion at low temperature seems to

[1] Ann. Chem. (Liebig), **106**, 30.

consist in the formation of the symmetrical dichloride, the reaction of the mass could be explained by assuming it to be a mixture of the anhydride and this chloride with some acid.

Different samples of the anhydride obtained by the described method were analyzed :

I.   0.1306 gram gave 0.2166 gram CO_2 ; 0.0300 gram H_2O.
II. 0.1567 gram gave 0.2611 gram CO_2 ; 0.0330 gram H_2O.
III. 0.1828 gram gave 0.3065 gram CO_2 ; 0.0389 gram H_2O.
IV. 0.2012 gram gave 0.2543 gram $BaSO_4$ (Liebig).

	Calculated for $C_7H_4SO_4$.	I.	II.	III.	IV.
			Found.		
C	45.64	45.23	45.44	45.58	....
H	2.17	2.56	2.34	2.36	....
S	17.39	....	....	....	17.39

The combustions were made with lead chromate mixture. Analysis I was made by Mr. E. S. Smith of this laboratory.

By the described method the anhydride is easily obtained in large, clear, colorless, monoclinic crystals, usually showing a prism and basal plane, sometimes a small orthopinacoid; cleavage prismatic.

The anhydride absorbs moisture quite rapidly if powdered or in small crystals, deliquescing to a sirup of orthosulphobenzoic acid. Large whole crystals are more stable, but become dull, and finally break down. It is soluble in anhydrous ether, benzene, or chloroform. Such solutions rapidly absorb moisture, and deposit crystals of orthosulphobenzoic acid. The melting-point of the pure anhydride is 129.5°. It sublimes apparently at or below its melting-point and can be distilled.

The anhydride may also be prepared in quantity by distilling the acid with phosphorus pentoxide.

Action with Alcohol.

Alcohols dissolve the anhydride with the formation of acid esters of orthosulphobenzoic acid. Similar esters were prepared by Remsen and Dohme[1] by the action of alcohols on the chloride. They ascribed the general formulæ given on account of the general properties and the ability to form chloroesters.

[1] This JOURNAL, **11**, 341.

Methyl Alcohol.—When the anhydride is treated with methyl alcohol (absolute or 98 per cent.) it dissolves with evolution of heat. On evaporating the alcoholic solution a thick sirup is obtained, which slowly crystallizes in needles, exceedingly deliquescent and soluble; they could not be obtained in any amount:

$$C_6H_4\!\!\begin{array}{c} CO \\ SO_2 \end{array}\!\!\!\!>\!\!O + CH_3OH = C_6H_4\!\!\begin{array}{c} CO.OCH_3 \\ SO_2OH \end{array} + H_2O.$$
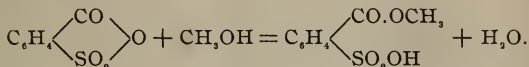
The acid methyl ester has been described by Remsen and Dohme[1] and by Karslake.[2]

The *silver salt* was obtained by dissolving silver carbonate in the solution of the acid methyl ester. It crystallized from concentrated solution in methyl alcohol, in plates, the solution darkening considerably on exposure.

Of the crystals: 0.2005 gram gave 0.0663 gram metallic silver equivalent to 33.65 per cent. silver.

The formula $C_6H_4\!\!\begin{array}{c} CO.OCH_3 \\ SO_2OAg \end{array}$ requires 33.4 per cent.

The *potassium salt* was similar to that described by Remsen and Dohme.

0.1480 gram gave 0.1422 gram $BaSO_4$ (Liebig method).
0.1638 gram gave 0.0563 gram K_2SO_4.

	Calculated for $C_7H_4SO_3.OC_2H_5.OK$.	Found.
S	12.59	12.51
K	15.39	15.50

Ethyl alcohol dissolves the anhydride easily, the alcoholic solution evaporating to a sirup, like the corresponding methyl compound, showing crystallization.

The *potassium salt*, $C_6H_4\!\!\begin{array}{c} CO.OC_2H_5 \\ SO_2.OK \end{array}$, crystallizes in pearly plates and is very soluble.

0.2010 gram gave 0.0649 gram K_2SO_4, equivalent to 14.48 per cent. K; above formula requires 14.58 per cent.

[1] This JOURNAL, **11**, 332.   [2] Dissertation J. H. U., 1895.

The *silver salt*, $C_6H_4\begin{cases} SO_2.OAg \\ CO.OC_2H_5 \end{cases}$, crystallizes in deliquescent needles.

0.1243 gram gave 0.0395 gram silver equivalent to 31.76 per cent.

Action with Phenols.

By the action of phenols on the anhydride, sulphonphthaleïns were obtained in pure condition without difficulty. Some of these substances, especially the resorcinol derivatives, have been extensively studied in this laboratory.[1] By treating the free acid with phenols in presence of dehydrating agents, White obtained colored products, but not in any amount or in pure condition. Under the conditions employed by him the anhydride must have been present, and the failure to obtain better results can only be attributed to the temperatures employed.

The phthaleïns under certain conditions decompose on being heated, generally at about 150° with evolution of hydrogen sulphide. In this work it was found necessary to keep the temperature between 130° and 135°; below this, as a rule, the operation did not progress well; at higher temperatures decomposition often occurred, products being formed generally darker and less soluble than the sulphonphthaleïns, soluble in alkalies with only slight colors, not to be compared with those of the sulphonphthaleïns. These products were not further investigated.

The sulphonphthaleïns described were all produced by the direct action of the phenol and anhydride at temperatures between 130°–138°. The use of dehydrating agents was found to be unnecessary and objectionable, the yield being decreased by loss incurred in separating the dehydrating agent.

The following was the general method employed: The anhydride was mixed with somewhat more than twice the molecular equivalent of the phenol, in a porcelain crucible, and the mixture heated in an air-bath at 130°–135° for about twenty-four hours, with frequent stirring. The dark mass generally

[1] This JOURNAL, **11**, 73; **14**, 455; **16**, 513, 528; **17**, 545, 556.

still had the odor of phenol, and showed green fluorescence. The mass was disintegrated with hot water, and boiled (until free from phenol or cresol), and concentrated so that most of the sulphonphthaleïn crystallized out on cooling.   It was then filtered and washed with water; the filtration is slow and difficult and must be aided by suction.   This generally furnished the phthaleïn in pure condition, but often it was necessary to dissolve in alkali and reprecipitate by acids.   An amorphous powder was thus obtained exceedingly difficult to filter.   The loss is considerable, most of the washing being done by decantation.

An attempt was made to induce combination at lower temperatures by treating solutions of the anhydride and phenols with dehydrating agents; but only with resorcinol was a slight color observed.

When the anhydride and phenol (or cresol) are mixed, a red color is seen, but the reaction does not seem to continue.

The filtrates from the sulphonphthaleïns were examined but no evidence of the formation of benzoylbenzenesulphonic acids could be found.   The reaction takes place thus:

$$C_6H_4\diagdown^{CO}_{SO_2}\diagup O + 2C_6H_5OH = C_6H_4\diagdown^{C(C_6H_4OH)_2}_{SO_2}\diagup O + H_2O.$$
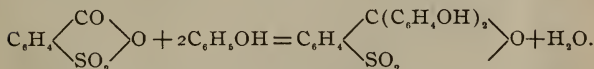
The sulphonphthaleins are intensely colored substances, more soluble in water than the corresponding derivatives of phthalic acid, and soluble in alcohol, from which they are precipitated in crystalline form by ether.

Varying the proportions did not alter the product, but only the rate of action and yield.
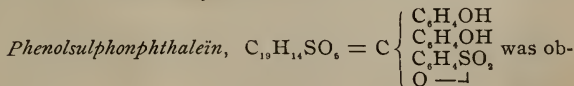
Phenolsulphonphthaleïn, $C_{19}H_{14}SO_5 = C\begin{cases} C_6H_4OH \\ C_6H_4OH \\ C_6H_4SO_2 \\ O \end{cases}$ was ob-

tained as a bright red crystalline powder, somewhat soluble in water, more so in alcohol, from which it was precipitated by ether as a yellowish-red crystalline powder, which on removal from the liquor instantly gave up ether, and solidified to a dark mass, which was apparently the same material.

The dilute alkaline solution is somewhat purer red than that of phenolphthaleïn; the more strongly alkaline solutions are purple. It is about as sensitive to alkalies and acids as phenolphthaleïn. The color does not disappear as readily on heating, and it might be used as an indicator with ammonia.

From the alkaline solution the sulphonphenolphthaleïn is precipitated as a dark red powder. By the slow cooling and evaporation of a solution in glacial acetic acid, the phenol-sulphonphthaleïn was obtained in distinct nodules of radiating needles, blue-green by reflected, and deep-red by transmitted light. On analysis the following results were obtained:

I. 0.2144 gram gave 0.5063 gram CO_2; 0.0876 gram H_2O.

II. 0.1669 gram gave 0.3656 gram CO_2, 0.0666 gram H_2O.

III. 0.2254 gram gave 0.1456 gram $BaSO_4$.

IV. 0.2247 gram lost 0.0028 gram at $135°$ = 1.23 per cent.

	Calculated for $C_{19}H_{14}SO_5$.	I.	Found. II.	III.
C	64.40	64.35	64.20	....
H	3.90	4.53	4.43	....
S	9.04	....	....	8.84

Phenolsulphonphthaline.—The alkaline solution of the sulphonphthaleïn was treated with zinc dust; the yellowish solution was filtered in an atmosphere of hydrogen, when, after the removal of the zinc, and most of the potassium salts, small granular crystals were formed, probably of the leuco base, di-hydroxytriphenylmethanesulphonic acid.

Dibromphenolsulphonphthaleïn, $C_{19}H_{12}Br_2SO_5$. — Phenolsul-phonphthaleïn, in glacial acetic acid, was treated with excess of bromine dissolved in glacial acetic acid; the acid was rapidly expelled by a current of air, and the bromine derivative deposited as a granular, purplish, crystalline powder.

0.2050 gram gave 0.0871 gram silver and 0.0983 gram $BaSO_4$ (Carius' method), equivalent to 31.47 per cent. bromine and 6.37 per cent. sulphur. $C_{19}H_{12}Br_2SO_5$ requires 31.25 per cent. bromine and 6.27 per cent. sulphur.

Dibromphenolsulphonphthaleïn gives a blue to purple color with alkalies. This color disappears on standing with excess of alkali, with formation of a green fluorescent solution. The

acid solution is yellow. It is extremely delicate as an indicator, is sensitive to ammonia, not sensitive to carbon dioxide, gives a decided blue color with tap water (hardness about $3°$).

An effort was made to prepare an acetyl derivative by boiling the phenolsulphonphthaleïn with acetic anhydride, but apparently none was formed; anhydrous ether added to the solution separated the peculiar precipitate above mentioned, which seemed to be the same substance.

Phenolsulphonphthaleïn was heated in a sealed tube with concentrated hydrochloric acid for five hours at $170°–180°$, but no action could be detected. On heating for two hours at $230°–240°$ decomposition was effected. Considerable pressure was observed on opening the tube; the liquid portion yielded only phenol and sulphur acids; the black solid residue yielded only a slight color to alkali, and was apparently carbon, yielding nothing on distillation.

In order to obtain a dihydroxytriphenylmethanesulphonic acid, the sulphonphthaleïn was boiled for fifty hours with hydrochloric acid, but no indication of such decomposition could be detected in the result. Boiling for fifty hours with excess of barium hydroxide also failed to produce any change. With dilute potassium hydroxide no action could be detected on boiling for a week; with concentrated caustic potash decomposition was effected in several hours, but the products could not be separated from the excess of alkali.

On heating the phenolsulphonphthaleïn in melted caustic potash the mass was found to contain sulphite, phenol, and a crystallizable substance identified as paradihydroxybenzophenone, as described by Baeyer and Burkhardt.[1]

$$C\begin{cases} C_6H_4OH \\ C_6H_4OH \\ C_6H_4SO_2 \\ O\text{---} \end{cases} + 2H_2O = C_6H_5OH + H_2SO_3 + CO\begin{cases} C_6H_4OH \\ C_6H_4OH \end{cases}.$$

Orthocresolsulphonphthaleïn, $C_{21}H_{18}SO_5 = C\begin{cases} C_6H_3.CH_3.OH \\ C_6H_3.CH_3.OH \\ C_6H_4SO_2 \\ O\text{---} \end{cases}$
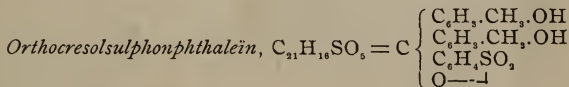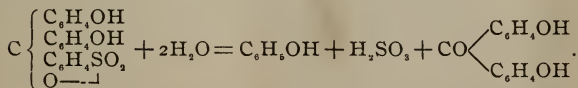
was obtained by the same method as the phenolphthaleïn. It

[1] Ann. Chem. (Liebig), **202**, 196.

crystallized from water, more easily than its lower homologue, appearing beetle-green by reflected and deep carmine by transmitted light. It is less soluble in water than the phenol compound, and the alkaline solutions are purple to carmine according to dilution, the neutral or dilute acid yellow, with strong acids, salmon color.

On analysis the following figures were obtained :

I. 0.1731 gram gave 0.4182 gram CO_2 ; 0.0755 gram H_2O.
II. 0.1558 gram gave 0.3762 gram CO_2 ; 0.0694 gram H_2O.
III. 0.2016 gram gave 0.1240 gram $BaSO_4$ (Liebig method).

	Calculated for $C_{21}H_{18}SO_5$.	I.	Found. II.	III.
C	65.99	65.90	65.85	....
H	4.71	4.85	4.95	....
S	8.37	....	....	8.45

Dibromorthocresolsulphonphthaleïn, $C_{21}H_{16}Br_2SO_5$, was obtained by treating the acetic acid solution with bromine; it resembles the phenol compound in color and general properties.

The analysis gave the following results :

I. 0.2051 gram gave 0.0804 gram Ag, and 0.0866 gram $BaSO_4$.

II. 0.2280 gram gave 0.0900 gram Ag, and 0.0962 gram $BaSO_4$.

	Calculated for $C_{21}H_{16}Br_2O_5$.	I.	Found. II.
Br	29.26	29.10	29.05
S	5.95	5.79	5.83

On boiling the orthocresolsulphonphthaleïn with acetic anhydride it lost most of its color, nor did the alkaline solution show the intense color immediately. The acetyl derivative appeared to be easily saponifiable, and was not isolated.

Paracresolsulphonphthaleïn was much more difficult to prepare than the ortho compound ; it was not obtained pure. It had a yellow color somewhat fluorescent.

$$\textit{Resorcinolsulphonphthaleïn,} \quad C_{19}H_{12}SO_6 = C \begin{cases} C_6H_3.OH \\ C_6H_3.OH \\ C_6H_4SO_2 \\ O \end{cases} > O.$$
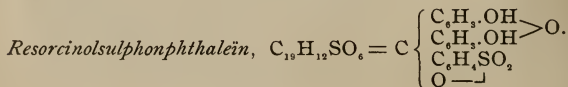
This substance could be produced much more easily and at lower temperature than the phenol derivatives. As shown by previous workers in this laboratory, resorcinol forms various condensation-products, all intensely colored fluorescent substances. It is worthy of note, however, that while Remsen and Linn[1] and Blackshear[2] produced only the diresorcinol derivative from the dioxybenzoylbenzenesulphonic acid, Remsen and McKee[3] produced the same substance from the chlorides, at low temperatures; at higher temperatures different derivatives are obtained.

In this work the materials were maintained at as low a temperature as possible to maintain action. The sulphonphthaleïn was obtained as a bright reddish-yellow powder, intensely fluorescent in alkaline solution. The color is more red than that of fluoresceïn, and is more quickly destroyed by excess of alkali. The bromine derivative is not as intense in color as eosin. Sulphonfluoresceïns have been described in detail by Remsen and Linn, and Blackshear.

Of the phthaleïn :

I. 0.1358 gram gave 0.3060 gram CO_2, and 0.0450 gram H_2O.

II. 0.2214 gram gave 0.1320 gram $BaSO_4$.

	Calculated for $C_{19}H_{12}SO_6$.	Found.
C	61.90	61.44
H	3.26	3.71
S	8.69	8.18

III. 0.3100 gram lost 0.0140 gram on heating at 135° for four hours, equivalent to 4.54 per cent.

IV. Dried in a desiccator, over sulphuric acid, 0.2024 gram lost 0.0057 gram at 130°, equivalent to 2.81 per cent. ; residue gave 0.0846 gram $BaSO_4$ (Liebig) equivalent to 5.73 per cent. sulphur.

V. Dried in air (eight weeks), 0.2043 gram lost 0.0094 gram at 135°, equivalent to 4.65 per cent. ; residue gave 0.0868 gram $BaSO_4$ (Liebig) equivalent to 5.82 per cent. sulphur. The odor of hydrogen sulphide was noticeable in the air-bath.

[1] This JOURNAL, **11**, 73.   [2] *Ibid*, **14**, 455.
[3] *Ibid*, **18**, 798.

Orcinolsulphonphthaleïn was formed easily and cleanly. It was not analyzed. It has been described in detail by Gilpin.[1]

Hydroquinolsulphonphthaleïn.—Hydroquinol reacted more slowly than resorcinol, and the mass as obtained by precipitation of the alkaline solution by acid, was dark brown and exceedingly difficult to filter. It is less soluble than the sulphonfluoresceïn, the alkaline solution being brown-yellow and not fluorescent.

I. 0.1930 gram gave 0.0158 gram $BaSO_4$, equivalent to 8.15 per cent. sulphur.

II. 0.1544 gram gave 0.0125 gram $BaSO_4$, equivalent to 8.04 per cent. sulphur.

The formula $C_{19}H_{14}SO_8$ requires 8.26 per cent. sulphur.

Pyrogallolsulphonphthaleïn (*Sulphongalleïn*), $C_{19}H_{10}O_8S$.— Pyrogallol reacts easily with the anhydride; the green product was disintegrated with much hot water, and purified by washing with water, and thus obtained as a blue-brown powder, somewhat soluble, giving a yellow to red color with acids, and an intense blue with alkalies, which rapidly became purple on exposure to the air, finally becoming a dirty green and brown, and depositing a brown precipitate. The addition of some stannous chloride to the alkaline solution preserves it for some time.

I. 0.2112 gram gave 0.1215 gram $BaSO_4$.

II. 0.2075 gram gave 0.1185 gram $BaSO_4$.

III. 0.1702 gram gave 0.3565 gram CO_2, and 0.040 gram H_2O.

	Calculated for $C_{19}H_{10}O_8S$.	I.	Found. II.	III.
C	57.28	....	....	57.12
H	2.51	....	....	2.60
S	8.14	7.89	7.84	....

An attempt to prepare the phthaline was unsuccessful, decomposition resulting.

m-Amidosulphonphthaleïn, $C_{19}H_{14}N_2O_4S$, was obtained as a reddish-brown powder, soluble in alkalies. These solutions are yellow, with a green fluorescence, by no means as strong as that of the sulphonfluoresceïn. Treatment with acetic anhydride failed to yield any derivative.

[1] This JOURNAL, **16**, 528.

0.2379 gram gave 0.210 gram BaSO$_4$, equivalent to 8.82 per cent. sulphur.

Formula C$_{19}$H$_{14}$N$_2$O$_4$S requires 8.74 per cent. sulphur.

p-Amidophenolsulphonphthaleïn isomeric with the above compound was obtained, impure, as a dark mass, more soluble than the sulphonrhodamine. It gave an intense blue-green with alkalies, red with acids, and is easily destroyed by oxidation in alkaline solution.

Salicylic acid melted with the anhydride yielded a bright-red coloring-matter.

Action with Ammonia.

The action of ammonia on the anhydride of orthosulpho-benzoic acid has been studied by Fahlberg and Barge and verified in the present work. Weber studied the action of ammonia on the anhydride of metasulphoparatoluic acid, and in both cases the result was the formation of the ammonia salt of the benzamine acid.

The anhydride was dissolved in anhydrous ether (or benzene) and dry ammonia gas passed into the solution with continual shaking, until thoroughly saturated. A white crystalline precipitate was formed; this was filtered off thoroughly and washed with anhydrous ether. Nothing was obtained from the ether but a little anhydride unacted upon.

The white substance was very soluble in water, from which it crystallized in nodules, and in alcohol from which it crystallized in needles; it is less soluble in absolute alcohol. It did not taste sweet, nor did it become sweet on heating, as sulphaminebenzoic acid does. In some cases a *faint* sweet taste was detected. It melted sharply at 256°–257°.

On analysis:

I. 0.2160 gram gave 0.0274 gram N (Kjeldahl).
II. 0.2511 gram gave 0.0151 gram N (by KOH).
III. 0.1531 gram gave 0.1638 gram BaSO$_4$.
IV. 0.1421 gram gave 0.1528 gram BaSO$_4$.
V. 0.1326 gram gave 0.1388 gram BaSO$_4$.

	Calculated for $C_7H_{10}SN_2O_4$.	I.	II.	Found. III.	IV.	V.
N_2	12.88	12.67	....	....	....	....
S	14.67	....	....	14.70	14.75	14.65
N by KOH	6.44	....	6.39	....	....	....

Determination V. was by Mr. E. E. Reid, of this laboratory. The reaction of the anhydride and ammonia may be represented :

$$C_6H_4\!\!\begin{array}{c}CO\\ \diagdown\\ SO_2\end{array}\!\!\!>\!O + 2NH_3 = C_6H_4\!\!\begin{array}{c}CONH_2\\ \diagdown\\ SO_2ONH_4\end{array}.$$
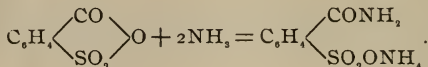
The result being the ammonium salt of benzaminesulphonic acid.

Barium benzaminesulphonate, $\left(C_6H_4\!\!\begin{array}{c}CONH_2\\ \diagdown\\ SO_2\end{array}\right)_2 Ba.5H_2O,$
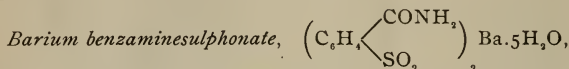
was obtained from the ammonium salt. It is very soluble in water, the solution evaporating to a thick syrup, and finally to a glass. From dilute alcohol it crystallized in white tufts or brittle needles. The same salt has been derived from cyan-benzenesulphonic acid described by Remsen and Karslake.[1]

I. 0.4360 gram lost 0.0627 gram at 140°, and gave 0.1625 gram $BaSO_4$.

II. 0.3532 gram lost 0.0513 gram at 140°, and gave 0.1316 gram $BaSO_4$.

	Calculated for $(C_7H_6NSO_4)_2Ba.5H_2O$.	Found. I.	II.
H_2O	14.35	14.15	14.52
Ba	21.85	22.05	21.92
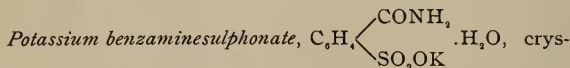
Potassium benzaminesulphonate, $C_6H_4\!\!\begin{array}{c}CONH_2\\ \diagdown\\ SO_2OK\end{array}\!\!.H_2O,$ crys-

tallized from dilute alcohol in small needles, easily soluble in water.

I. 0.2318 gram lost 0.0159 gram at 140° and gave 0.0784 gram K_2SO_4.

II. 0.1813 gram lost 0.0129 gram at 140° and gave 0.0633 gram K_2SO_4.

[1] This JOURNAL, **18,** 826.

| | Calculated for | Found. | |
	$C_7H_6SO_4NK.H_2O$.	I.	II.
H_2O	7.00	6.88	7.11
K	15.21	15.22	15.26

The potassium salt was treated with phosphorus pentachloride; the oily chloride thus obtained was decomposed by boiling with water, neutralized by ammonia, and crystallized in botryoidal crystals characteristic of the orthocyanbenzenesulphonic acid.

$$C_6H_4{<}^{CO.NH_2}_{SO_2OH} \longrightarrow C_6H_4{<}^{CN}_{SO_2Cl} \longrightarrow C_6H_4{<}^{CN}_{SO_2OH}.$$
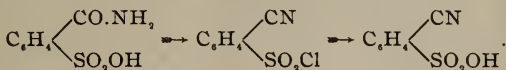
The barium benzaminesulphonate was titrated with sulphuric acid, filtered, and evaporated to a sirup; no crystals could be obtained. Fahlberg and Barge describe it as crystallizing in needles. Neither Jesurun[1] nor Remsen and Karslake[2] could obtain it in crystals.

Action with Aromatic Amides.

With aniline and toluidines the action was analogous to that with ammonia. The anhydride and base, dissolved in anhydrous benzene or ether, were mixed, when a pasty colorless mass separated. When equimolecular quantities were used, addition of more base produced further precipitation until a second equivalent of base had been added. The mass suspended in benzene, on long boiling, usually became hard and somewhat crystalline. It was well washed with benzene, and on treatment with water dissolved entirely.

By mixing the base and anhydride and heating, the same substances resulted, but they were usually darker and more difficult to purify.

On examination these substances proved to be the salt of the base with a benzanilido acid.

$$C_6H_4{<}^{CO}_{SO_2}{>}O + 2NH_2R = C_6H_4{<}^{CONHR}_{SO_2ONH_3R}.$$
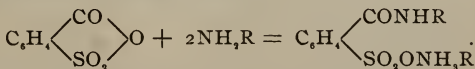
The general properties of the acids are the same. The acids are very soluble, none being obtained in crystallized

[1] Ber. d. chem. Ges., **26**, 2288.　　　[2] *Loc. cit.*

state, in marked distinction to the isomeric sulphanilido acids. The salts crystallize slowly from concentrated solution ; often they separate as an oil, which becomes crystalline only on very long standing, and some also become liquid before dissolving.

In neutral solution they are generally stable, but often become discolored in the light. They are decomposed by long boiling with acids or strong alkali, with separation of the base, and formation of orthosulphobenzoic acid.

$$C_6H_4\Big\langle{}^{CO.NHR}_{SO_2OH} + H_2O \rightarrow C_6H_4\Big\langle{}^{CO_2H}_{SO_3H} + NH_2R.$$
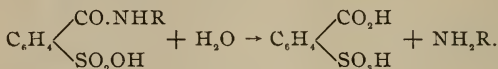
With phosphorus pentachloride the corresponding sulphinide derivative is formed :

$$C_6H_4\Big\langle{}^{CONHR}_{SO_2OH} + PCl_5 \rightarrow C_6H_4\Big\langle{}^{CO}_{SO_2}\Big\rangle NR + HCl + POCl_3.$$
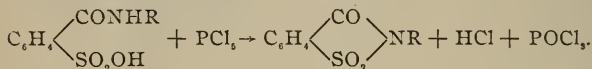
These have been described by Remsen and Coates,[1] and by Remsen and Kohler, and are decomposed on boiling with alkali, with formation of sulphanilido compounds, which are less soluble and well crystallized.

Aniline Benzanilidosulphonate, $C_6H_4\Big\langle{}^{CO.NHC_6H_5}_{SO_2ONH_3C_6H_5}$, was

the only product obtained by the action of aniline on the anhydride. The mass as obtained was exceedingly soluble in water and in alcohol; insoluble in benzene and ether. On direct evaporation of the concentrated solution an oil or paste was obtained, which would not crystallize, and darkened on exposure to light and air. On slow evaporation of a solution in dilute alcohol *in vacuo*, or better over sulphuric acid, white tufts of radiating needles were obtained. These gave the reactions for aniline, and were very soluble and difficult to crystallize. They did not lose weight on heating to 140°, but began to turn dark green.

I. 0.2056 gram gave 0.1276 gram $BaSO_4$ (Carius method).
II. 0.1851 gram gave 0.1144 gram $BaSO_4$ (Carius method).
III. 0.2621 gram gave 0.0203 gram N (Kjeldahl).

	Calculated.	I.	II.	III.
S	8.64	8.52	8.49	....
N	7.84	....	....	7.75

Barium Benzanilidosulphonate $\left(C_6H_4\!\!\begin{array}{l}CO.NHC_6H_5\\SO_2O\end{array}\right)_2 Ba.$
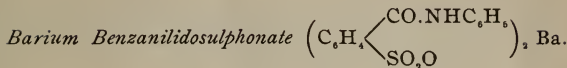
$5H_2O$, is very soluble in water, and could not be crystallized
from it. The solution evaporated to a hard transparent glass.
From dilute alcohol it crystallized in fine, radiating, chalky
needles. It is very soluble in water although the crystals
dissolve but slowly.

I. 0.2211 gram lost 0.0258 gram and gave 0.0658 gram
$BaSO_4$.

II. 0.2131 gram lost 0.0262 gram and gave 0.0638 gram
$BaSO_4$.

	Calculated for $(C_{13}H_{10}NO_4S)_2Ba.5H_2O$.	I.	Found. II.
Ba	17.38	17.51	17.61
H_2O	11.55	11.67	11.81

Ammonium Benzanilidosulphonate, $C_6H_4\!\!\begin{array}{l}CONHC_6H_5\\SO_2ONH_4.H_2O\end{array}$,
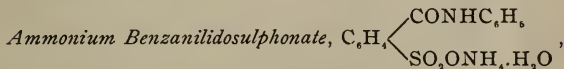
is very soluble in water, and crystallized quite readily in
silky, radiating needles.

I. 0.2112 gram gave 0.0106 gram NH_3.

II. 0.2326 gram lost 0.0133 gram at 130°, and gave 0.1745
gram $BaSO_4$.

	Calculated for $C_{13}H_{14}N_2SO_4.H_2O$.	I.	Found. II.
H_2O	5.76	....	5.75
S	10.25	....	10.27
NH_3	5.45	5.50	....

Potassium Benzanilidosulphonate, $C_6H_4\!\!\begin{array}{l}CO.NH.C_6H_5\\SO_2OK.H_2O\end{array}$,
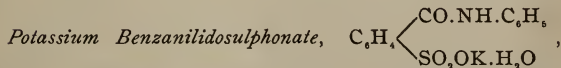
slowly separated from dilute alcoholic solution in fine silky
crystals.

I. 0.2762 gram lost 0.0165 gram at 130°, gave 0.0691 gram
K_2SO_4.

II. 0.2516 gram lost 0.0139 gram at 140°, gave 0.0651 gram
K_2SO_4.

	Calculated.	I.	II.
H_2O	6.00	5.94	5.52
K	11.73	11.22	11.50

The *cadmium* salt separated as a poorly crystalline powder.

I. 0.2920 gram gave 0.2015 gram $BaSO_4$.

II. 0.2265 gram gave 0.0398 gram CdO.

	Calculated.	Found.
Cd	16.83	16.70
S	9.63	9.48

The *sodium*, *copper* and *lead* salts evaporated to hard glasses, and the *silver* salt decomposed on evaporation.

The *free acid* was obtained from the lead salt (by hydrogen sulphide) as a thick sirup ; neither water nor alcoholic solution showed any sign of crystallization within three months.

Action of Phosphorus Pentachloride.—The potassium salt was treated with phosphorus pentachloride ; on adding water a white solid separated. This was washed with water and proved to be free from chlorine. It crystallized from alcohol in flat needles ; on recrystallization from ether it melted sharply at 190°–191° (uncorr.). It was insoluble in acid, and in cold alkali ; dissolved by boiling alkali and precipitated by acids. This, crystallized from hot water, had the melting-point 159° (uncorr.) ; corresponding to the anil and sulphanilido acid, the action of the pentachloride being therefore one of dehydration :

$$C_6H_4\!\!\begin{array}{c}\diagup CONHC_6H_5 \\ \diagdown SO_2OH\end{array} \rightarrow C_6H_4\!\!\begin{array}{c}\diagup CO \\ \diagdown SO_2\end{array}\!\!\!\!>\!\!NC_6H_5.$$
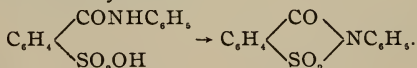
Equimolecular quantities of aniline and anhydride were heated with phosphorus pentoxide at 180°. The mass darkened considerably ; and from it a substance crystallizing like the anil from alcohol and chloroform was obtained. It could not be obtained free from the product of decomposition ; its melting-point was about 176°. By long heating with acid, or more quickly by heating to 170° with hydrochloric acid, the anilido acid is converted into orthosulphobenzoic acid.

Paratoluidine Benzparatoluidoorthosulphonate,

$$C_6H_4\!\!\begin{array}{c}\diagup CO.NHC_7H_7 \\ \diagdown SO_2NH_2C_6H_7\end{array}$$
.—As in the case of aniline apparently
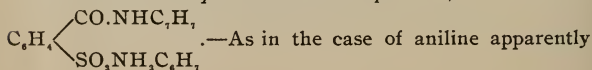
only one substance was formed by action of paratoluidine. The mass as obtained was very soluble in hot water, and separated on cooling as a thick oil, which on long standing (six or eight weeks) covered by water, slowly began to crystallize. The crystals first appearing were removed from the oil to another part of the beaker and grew in small clusters as short, sharply-pointed needles.

I. 0.1530 gram gave 0.0111 gram N (Kjeldahl).
II. 0.1402 gram gave 0.0826 gram $BaSO_4$.

	Calculated.	I.	II.
S	7.98	....	8.10
N	6.97	7.25	...

Barium Benztoluidosulphonate crystallized in radiate nodules, sometimes forming a crust on the sides of the beaker and on top of the liquid. Successive crystallization indicated that it was a basic salt, and no formula could be calculated from the analyses:

I. 0.3848 gram lost 0.0260 gram at 150° and gave 0.1199 gram $BaSO_4$.
II. 0.4186 gram lost 0.0280 gram at 150° and gave 0.1312 gram $BaSO_4$.

	I.	II.
Ba	18.34	18.43
H_2O	6.75	6.80

Potassium Salts, $C_6H_4 \Big\langle {CONKC_7H_7 \atop SO_2OK.H_2O}$ and $C_6H_4 \Big\langle {CONH.C_7H_7 \atop SO_2OK.H_2O}$.
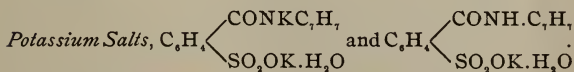
These salts crystallized in radiating clusters, and were separated by fractional precipitation of the alcoholic solution by ether. The former salt was obtained pure, the latter not.

I. 0.3233 gram lost 0.0161 gram at 140°.
II. 0.2720 gram lost 0.0134 gram at 140° and gave 0.1238 gram K_2SO_4.
III. 0.2190 gram gave 0.0975 gram K_2SO_4.

	Calculated for $C_{14}H_{11}SO_4K_2.H_2O$.	I.	Found. II.	III.
H_2O	4.70	4.97	4.93	....
K	20.20	....	20.41	19.93

The free *benztoluidosulphonic acid* was obtained, by treating the barium salt with sulphuric acid, as a thick uncrystallizable mass.

Action of Phosphorus Pentachloride.—The potassium salt was treated with phosphorus pentachloride, and the mass treated with water. The resulting substance was crystallized from alcohol and identified as the paratolil described by Remsen and Coates.[1] By heating with acid at 180° the salts are converted into salts of orthosulphobenzoic acid.

Orthotoluidine Benzorthotoluidoorthosulphonate,

$$(o)C_6H_4 \Big\langle \begin{matrix} CO.NH.C_7H_7\ (o) \\ SO_2.ONH_3C_7H_7\ (o) \end{matrix} \Big. , \text{ was formed by the action of}$$

the anhydride upon orthotoluidine. The salt crystallized more readily than the analogous para compound, in nodules of radiating needles.

I. 0.2455 gram gave 0.1520 gram $BaSO_4$.
II. 0.2069 gram gave 0.1235 gram $BaSO_4$.
III. 0.2233 gram gave 0.1312 gram $BaSO_4$.
IV. 0.2013 gram gave 0.0112 gram N (Kjeldahl).

	Calculated for $C_{21}H_{22}N_2SO_4$.	I.	Found. II.	III.	IV.
S	7.98	8.50	8.19	8.07	....
N	6.97	....	....	....	6.70

Barium Benztoluidosulphonate crystallized in radiating nodules. It was probably a mixture of a basic salt and the normal. No simple formula could be calculated.

$$\text{*Potassium Benztoluidosulphonate*, } C_6H_4 \Big\langle \begin{matrix} CO.NHC_7H_7 \\ SO_3K \end{matrix} \Big. , \text{ crys-}$$

tallized in sharply-pointed, brittle, white needles in nodules.

I. 0.2010 gram gave 0.0538 gram K_2SO_4.
II. 0.3227 gram gave 0.0870 gram K_2SO_4.
III. 0.2607 gram gave 0.0725 gram K_2SO_4.

	Calculated.	I.	II.	III.
K	11.88	12.01	12.09	12.49

There was also a potassium salt probably analogous to the

[1] *Loc. cit.*

one described under the paratoluidine derivatives, but it could not be obtained in pure condition.

On heating the salts with acid at 180°, they are converted to salts of orthosulphobenzoic acid.

The potassium salt was treated with phosphorus penta-chloride, and on treating the mass with water, a substance was obtained, which on recrystallization from alcohol, melted at 170° (uncorr.) and was identified as the orthotolil described by Remsen and Coates.

Acid Amides.

Benzamide was boiled with the anhydride in benzene solution. Small crystals (prisms) separated, and the odor of nitrile was noticed. The mass after removal of the benzene was boiled with water, and, on cooling, crystals separated which were identified as benzoic acid. The solution was found to contain the acid ammonium salt of orthosulphobenzoic acid. Nothing else could be found. The action is that of dehydration :

$$C_6H_4 \diagdown \begin{matrix} CO \\ SO_2 \end{matrix} \diagup O + C_6H_5CO.NH_2 \longrightarrow C_6H_5CN + C_6H_4 \diagdown \begin{matrix} CO.OH \\ SO_2OH \end{matrix}$$

$$C_6H_5CN + 2H_2O \longrightarrow C_6H_5COOH + NH_3.$$
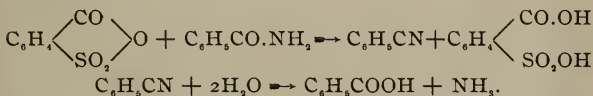
Acetamide acted like benzamide but with more difficulty,

$$CH_3CONH_2 - H_2O \longrightarrow CH_3CN.$$

Phosphorus pentachloride acting on the anhydride produced both chlorides of orthosulphobenzoic acid. The action was exceedingly variable, depending upon the purity of the chemicals, the temperature and time of action. With pure dry chemicals it was impossible to secure action below 120°. A small amount of oxychloride considerably lowered the temperature. At 20° no action took place even though the mass was moistened with phosphorus oxychloride.

It was concluded from numerous experiments that the formation of the *unsymmetrical chloride* was favored by high temperature, continued action and excess of pentachloride. The same results were noted in the action of the pentachloride on the potassium salts.

Conclusion.

In the foregoing it has been shown that the anhydride of orthosulphobenzoic acid is a well-characterized stable substance.

Many of the sulphonphthaleïns are readily obtained in pure condition, and they are possessed of marked color, analogous to the phthaleïns, which they resemble.

A series of sulphonic acids has been formed isomeric with the sulphaminebenzoic acids from which they are distinguished by their solubility, and into which they can be converted by the successive action of phosphorus pentachloride and alkaline hydroxide.

XIX.—IODOMETRIC ESTIMATION OF TELLURIUM.

By JAMES F. NORRIS AND HENRY FAY.

Tellurium is estimated accurately with difficulty. Of the two gravimetric methods, weighing as the dioxide and in the elementary state, the former alone is accurate. When determined as the dioxide, tellurium is separated from other elements and oxidized with dilute nitric acid. After evaporation of the solution to dryness the basic nitrate is transferred to a crucible and heated to fusion. On account of the time required the determination is shortened by weighing the precipitated tellurium after drying at 110°. Brauner[1] has shown, however, that the results obtained in this way are not reliable. The finely divided tellurium is slowly oxidized in the strong hydrochloric acid solution required for the precipitation with sulphur dioxide, forming tellurium tetrachloride which remains in solution. When tellurium is washed and dried it slowly oxidizes and the weight found is, consequently, too great. It was shown that precipitated tellurium increased in weight about 0.5 per cent. during washing and drying for two hours at 110°. As these two sources of error tend to neutralize each other, the result obtained is approximately correct.

[1] J. Chem. Soc., **55**, 392.

Brauner[1] has made a careful study of a number of reactions of tellurium with the view of using them for its volumetric estimation. He found that the reactions between tellurium dioxide and stannous chloride, potassium bichromate, iodine, or potassium permanganate in acid solution, could not be made the basis of an accurate method, but that the oxidation of tellurium dioxide with potassium permanganate in alkaline solution proceeded regularly. The excess of permanganate was determined, after acidifying with sulphuric acid, by adding an excess of oxalic acid and titrating back with permanganate. When the solution was acidified part of the permanganate was decomposed and oxygen and ozone were liberated. The amount of decomposition depends upon the quantity of sulphuric acid used and upon the concentration of the solution. Brauner found that by working under definite conditions there was a constant source of error which amounted to 0.35 per cent., and by deducting this amount satisfactory results could be obtained. This method cannot be used in the presence of the halogen acids.

Gooch and Morgan[2] have recently proposed a method for the estimation of tellurium based on the insolubility of the iodide in strong sulphuric acid. To the solution of tellurium dioxide is added sulphuric acid in such quantity, that after mixing with the potassium iodide solution the concentration of the acid is not less than 25 per cent. by volume. A standard solution of potassium iodide is added until no further precipitation takes place. The results are fairly accurate when less than 0.1 gram of tellurium dioxide is used for analysis.

As work requiring the rapid estimation of tellurium in presence of the halogen acids is in progress in this laboratory, a new method was sought. The method recently proposed by us[3] for selenium was applied to tellurium. It was shown that one molecule of selenous acid reacts with four of sodium thiosulphate in the presence of dilute acids. A similar reaction takes place with tellurous acid but the end-point is not sharp, because the addition of sodium thiosulphate produces a yel-

[1] J. Chem. Soc., **59**, 58, 238.   [2] Ztschr. anorg. Chem., **13**, 169.
[3] This JOURNAL, **18**, 703

low solution, and the reduced tellurium compound is slowly oxidized by iodine. By observing the first appearance of a greenish color, however, the amount of tellurium dioxide could be approximately determined.

As the results were not positive, another method was studied, namely, oxidation of tellurous to telluric acid by potassium permanganate and estimation of the excess of the latter by treating with potassium iodide and sulphuric acid, and titrating the liberated iodine with sodium thiosulphate. Brauner has shown that the oxidation of tellurous acid to telluric acid in alkaline solution takes place according to the following equation:

$$(1) \quad 2KMnO_4 + 3TeO_2 = K_2O + 2MnO_2 + 3TeO_3.$$
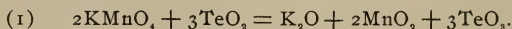
The manganese dioxide is not precipitated, but remains in solution, probably as a manganite or in combination with telluric acid, forming a compound analogous to the salt $MnO_2.SO_3$. If to such a solution potassium iodide and sulphuric acid be added, the following reaction takes place:

$$(2) \quad 2MnO_2 + 4KI + 4H_2SO_4 = 2MnSO_4 + 2K_2SO_4 + 4H_2O + 4I.$$
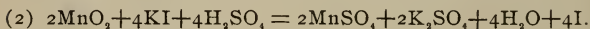
Any excess of permanganate will react as follows:

$$(3) \quad 2KMnO_4 + 10KI + 8H_2SO_4 = 2MnSO_4 + 6K_2SO_4 + 8H_2O + 10I.$$
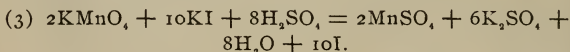
Combining equations (1) and (2) the oxidation of tellurium dioxide may be expressed in this way:

$$(4) \quad 2KMnO_4 + 3TeO_2 + 4KI + 5H_2SO_4 = 3TeO_3 + 3K_2SO_4 + 2MnSO_4 + 5H_2O + 4I.$$
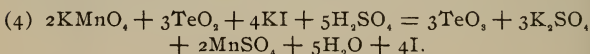
It is seen from equation (4) that 2 molecules of potassium permanganate in the presence of tellurium dioxide will liberate 4 atoms of iodine, whereas from equation (3) the same amount of permanganate will liberate 10 atoms of iodine. There is, therefore, a deficit of 6 atoms of iodine for 3 molecules of tellurium dioxide, or 1 molecule of the latter produces a deficit of 2 atoms of iodine, or 2 molecules of sodium thiosulphate. This deficit is obtained by subtracting from the amount of thiosulphate equivalent to the permanganate, equation (3), the amount required to react with the

iodine liberated in the presence of tellurium dioxide. This method gives accurate results, can be used in the presence of halogen acids, and does not require a factor-correction for the decomposition of the potassium permanganate.

Certain precautions are necessary in order that accurate results may be obtained ; the oxidation must take place in the presence of a large excess of alkali, and the solution must be dilute and cold in order to prevent the reduction of the telluric acid by the hydriodic acid.

The tellurium dioxide used to test the method was prepared in the following manner : A sample of tellurium containing traces of copper and selenium was precipitated with sulphurous acid, oxidized with nitric acid, evaporated to dryness, and fused. The oxide so obtained was dissolved in hot sodium hydroxide and precipitated with grape-sugar. The tellurium was again oxidized, and from the oxide the basic nitrate was obtained by crystallization from nitric acid (sp. gr. 1.25). After two crystallizations the basic nitrate, which was obtained in well-developed crystals 5–6 mm. in length, was decomposed into the oxide just below red heat. The resulting white powder was fused quickly in small portions. In this way pure, perfectly white, tellurium dioxide was obtained. Staudenmaier[1] states that it is difficult to get tellurium dioxide without a brown color, due to a minute trace of free tellurium. Fusion of the nitrate directly always causes the separation of traces of tellurium, but by proceeding as directed above, decomposing below a red heat, and then fusing, the oxide can be obtained in pure condition. A standard solution of the oxide was made by dissolving about 2.5 grams in a small amount of sodium hydroxide and diluting to 500 cc.

An approximately one-tenth normal solution of sodium thiosulphate was standardized against iodine, which had been dried over sulphuric acid and sublimed from one-third of its weight of potassium iodide. 1 cc. $Na_2S_2O_3 = 11.21$ mg. I.

A solution of potassium permanganate was made by dissolving about 7 grams of the salt in 1 liter of water. This was titrated against sodium thiosulphate in the following manner : To 20 cc. of the potassium permanganate, diluted

[1] Ztschr. anorg. Chem., **10**, 206.

to 400 cc. with ice-water, were added 10 cc. of a solution of potassium iodide, containing 2 grams of the salt, and dilute sulphuric acid until the solution became clear. The iodine liberated was equivalent to 49.90 cc. of sodium thiosulphate. In order to determine whether the reaction between potassium permanganate and potassium iodide in acid solution takes place as represented by equation (3), the permanganate was standardized against acid potassium oxalate. The same value was obtained by both methods.

In estimating tellurium a portion of the standard solution of the oxide was measured off and about 20 cc. of a 10 per cent. solution of sodium hydroxide added. Potassium permanganate was added until the meniscus of the brown solution showed a deep pink color. The solution was diluted with ice-water, treated with potassium iodide and sulphuric acid, and titrated as above.

The results obtained by this method, together with the amount of solutions used, are given in the following table. The quantity of sodium thiosulphate in each case is the amount equivalent to the iodine set free in the presence of tellurium dioxide. By subtracting these values from the amount equivalent to the potassium permanganate used, the deficit is obtained. $1 TeO_2$ causes a deficit of $2 Na_2S_2O_3$:

TeO_2 taken. Gram.	$KMnO_4$. cc.	$Na_2S_2O_3$. cc.	TeO_2 found. Gram.	Te. Per cent.
0.1507	20	28.58	0.1504	79.80
0.1507	20	28.55	0.1506	79.91
0.1758	25	37.39	0.1762	80.15
0.1758	25	37.48	0.1756	79.86
0.2009	30	46.38	0.2008	79.93
0.2009	30	46.40	0.2007	79.88
0.1562	20	27.79	0.1560	79.84
0.1824	25	36.50	0.1825	80.00

Theory, 79.94

The first six results were obtained by using portions of the standard solution of tellurium dioxide ; the last two by using portions weighed directly. The table contains a series of eight consecutive determinations. In calculating the results, 127.6 has been taken for the atomic weight of tellurium.

In order to test the accuracy of the method in the presence of the halogen acids, the double bromide of tellurium and potassium was analyzed. The salt was prepared by dissolving the theoretical quantities of tellurium dioxide and potassium bromide in hydrobromic acid and evaporating to crystallization. After recrystallization from a hot saturated solution the salt was dried at 120° for three hours. The following is a series of consecutive results :

K_2TeBr_6 taken. Gram.	$KMnO_4$. cc.	$Na_2S_2O_3$. cc.	Te. Per cent.
0.8823	30	45.62	18.59
0.7134	25	38.79	18.64
0.5472	20	31.88	18.58
0.5679	20	31.11	18.66

Theory, 18.61

A series of experiments showed that this method of analysis could also be applied to the determination of selenium, but it offers no advantages over the simpler method already proposed by us.

Boston, Mass., January, 1898.

THE RELATION OF TRIVALENT TO PENTAVALENT NITROGEN.

By Arthur Lachman.

The following lines contain a preliminary account of a few experiments undertaken for the purpose of investigating the subject of this brief paper. The experiments are fragmentary, but for the present I cannot continue them. In publishing this note, I wish to secure for myself the right to take up the work again as soon as I can find the opportunity to do so.

The idea is by no means new that the peculiarities of nitrogen compounds may find their explanation in the variability of the valence of their nitrogen atoms. Innumerable well-known facts illustrate the tendency of nitrogen to pass from one state of valence to the other. Indeed, most attempts to explain the reactions of nitrogen compounds are based upon the assumption of some such relation. While many of these speculations rest upon a tolerably safe foundation, many

others are very vague ; nearly all have one feature in common; *viz.*, arbitrariness. The following experiments were undertaken for the purpose of determining the actual limits within which such speculations must remain.

For certain theoretical reasons, which need not be discussed as yet, the secondary nitrosamines were first taken up. These substances contain, in all likelihood, two trivalent nitrogen atoms of diverse chemical character, $R_2 = \overset{\text{III}}{N} - \overset{\text{III}}{N} = O$, and, therefore, seemed to afford a good starting-point for the study of addition reactions. So far, their behavior towards hydrochloric acid, zinc ethyl, and hydroxylamine has been investigated.

Nitrosamines with Hydrochloric Acid.

Both dimethyl- and diethylnitrosamine form hydrochlorides.[1] These salts are very unstable, and at a slightly elevated temperature break down. On heating them in a sealed tube to about 60°, the tube becomes filled with deep-red fumes, and upon cooling down, crystals of dimethyl- (or diethyl-) amine hydrochloride appear. If a rapid stream of hydrochloric acid gas is passed into diethylnitrosamine, the liquid becomes hot, nitrosyl chloride passes off, and diethylamine hydrochloride remains behind, the nitrosamine being completely decomposed :

$$\begin{matrix} C_2H_6 \\ C_2H_6 \end{matrix} \bigg\rangle NH + NOCl.$$
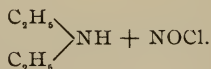
More interesting results were obtained with diphenylnitrosamine. A solution of this substance in benzene (carefully dried over sodium) was treated with a mixture of hydrochloric acid gas and carbon dioxide (both dried over phosphorus pentoxide). The carbon dioxide served to exclude the air and to moderate the action. The vessel containing the nitrosamine was kept cooled with water, and the gases emerging from it conducted into a solution of potassium iodide. The gas finally escaping turned brown in the air, showing that it con-

[1] Dimethylnitrosamine hydrochloride has been described by Renouf (Ber. d. chem. Ges., **13**, 2170). The salt of diethylnitrosamine is an oil which solidifies below 0°.

tained nitric oxide. The iodine set free was titrated with sodium thiosulphate:

1.00 gram nitrosamine required 24.5 cc. 1/5 N thiosulphate.

	Gram.
Iodine calculated	0.641
" found	0.622

It will thus be seen that very nearly the calculated amount of iodine was set free, showing that at the ordinary temperature diphenylnitrosamine takes up *dry* hydrochloric acid, and immediately splits off nitrosyl chloride:

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \!\!> \!\! \underset{NO}{\overset{v}{N}} \!\! <\!\! \begin{matrix} H \\ Cl \end{matrix} = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \!\!> \!\! NH + NOCl.$$
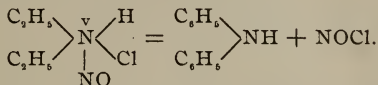
The residue in the flask formed a black tar, and no attempt was made to find diphenylamine in it.

The combination, $R_2 \!=\! N \!\!< \!\! \begin{matrix} H \\ Cl \\ NO \end{matrix}$, then, is a very unstable one, and readily breaks down into simpler molecules containing trivalent nitrogen. This is in exact analogy with the addition-products of the isonitriles discovered by Nef, in which the bivalent carbon atom readily takes up various substances, and as readily splits them off.

Nitrosamines with Zinc Ethyl.

Diethylnitrosamine does not react with zinc ethyl in the cold, even after standing several weeks. On warming to 100°, reaction takes place rapidly, accompanied by almost complete decomposition. Basic gases are given off, and a tarry substance remains which has basic properties, reduces silver nitrate, and does not yield crystalline derivatives.

Diphenylnitrosamine reacts violently with zinc ethyl in the cold. If the reaction is carried out in dilute benzene solution, with molecular quantities of the substances, the solvent soon becomes warm, and frequently boils. The solution is kept boiling for about an hour, and then carefully evaporated in a stream of dry carbon dioxide. A gelatinous mass re-

mains, which crumbles to a yellow powder when rubbed on a porous plate. The powder is amorphous; it melts at about 135°, is insoluble in all ordinary solvents, and apparently is quite stable in air. It is an addition-product formed from one molecule each of the reacting substances:

0.2414 gram gave 0.626 gram zinc oxide upon ignition.

	Calculated for $(C_6H_5)_2N.NO.Zn(C_2H_5)_2$.	Found.
Zinc	20.8	20.3

Its constitution is at present unknown. On treatment with water or alcohol, the substance is decomposed *without* evolution of gas; the products are zinc hydroxide, diphenylamine (melting-point 53.5°; diphenylamine reaction) and an unstable base. This base is slightly volatile with water vapor, and reduces Fehling's solution in the cold; its hydrochloric acid solution gives off ethyl chloride on boiling. Possibly the structure is to be represented as follows, which would account for the formation of diphenylamine and a reducing base (diethylhydroxylamine?), as well as for the absence of gases upon decomposition with water:

$$(C_6H_5)_2 = N - N \underset{\overset{|}{C_2H_6}}{\overset{\overset{C_2H_5}{|}}{<}} \overset{O}{\underset{Zn.}{|}}$$
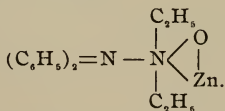
Here again we notice how readily a pentavalent nitrogen atom passes into the trivalent state. A number of other substances have been subjected to the action of zinc ethyl, but no report can be made as yet.

Nitrosamines with Hydroxylamine.

As a general rule, nitrosamines fail to show any condensation-reactions; their behavior with hydroxylamine seems to form an exception. The reaction of this substance with diethylnitrosamine is so curious, however, that I should prefer to wait for more evidence before presenting the facts.

Diphenylnitrosamine and hydroxylamine react quite readily. Though no new body could be isolated as the product, it was possible to follow the reaction quantitatively. If molecu-

lar quantities of the two substances are boiled in methyl-alcoholic solution, either in the presence or absence of free alkali, nitrous oxide is given off in theoretical quantity, and there remains only diphenylamine (19 grams from 25 grams nitrosamine ; calculated, 21 grams) :

1.0 gram nitrosamine gave 113 cc. moist nitrous oxide at 10° and 737 mm.

		Gram.
Nitrous oxide calculated		0.22
" " found		0.20

At no time during the reaction, which lasts from fifteen minutes to an hour (the more alkali present the shorter the duration), can any trace of hyponitrites be discovered, even in the presence of a very large excess (two molecules) of alkali. The appearance of nitrous oxide can therefore not be accounted for by the intermediate formation and decomposition of hyponitrous acid :[1]

$$(C_6H_5)_2=N—N=O+H_2NOH = (C_6H_5)_2NH+HON=NOH,$$

but only by the direct decomposition of the addition-product as indicated in the following formula :

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ \diagup \\ C_6H_5 \end{array} N — \begin{array}{c} v \diagup H \\ N=O \\ \diagdown N\,H.OH \end{array}$$
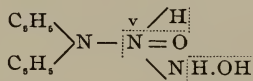
Again we have the curious splitting down of a pentavalent derivative of diphenylnitrosamine into the trivalent diphenylamine, at the low temperature of boiling methyl alcohol.

It is thus seen that very decided limits exist for the stability of pentavalent nitrogen compounds. By a proper choice of radicals, they may be made to break down spontaneously or upon very slight provocation. By continuing along the lines laid down, it will perhaps be possible to ascertain the nature and the amount of contrast among its attached groups of atoms which suffices to make the pentavalence of nitrogen unstable. On the other hand, we must not forget that a certain amount of diversity among the groups is necessary for the existence of the pentavalent state. No pentavalent nitrogen compound

[1] Since hyponitrites are stable in the presence of alkali.

is known in which all five radicals are alike in chemical character. An attempt to prepare such a compound, about two years ago,[1] proved abortive ; renewed efforts in the same direction have borne no results. The pentavalence of nitrogen, then, is determined by the contrast of the attached groups of atoms, it being possible to have too little as well as too much of this *sine qua non*. The work will be taken up again as soon as possible. This brief note is *not* intended to "reserve the field," but on the contrary to urge others to help in its cultivation.

EUGENE, OREGON, Jan., 1898.

ON PARAMETHOXYORTHOSULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

BY P. R. MOALE.[2]

Preparation.

The preparation of the above acid involves several stages, the starting-point being paratoluidineorthosulphonic acid. The directions of Parks[3] were followed in the main ; when differences occur, mention of them is made. Parks found that only the methoxy product was formed when paradiazoorthotoluenesulphonic acid, $C_6H_3 \begin{subarray}{l} \diagup CH_3 \\ -SO_3(2) \\ \diagdown N_2(4) \end{subarray}$, is boiled with absolute methyl alcohol under ordinary, diminished, or increased pressure. So the diazo compound prepared according to the directions of Parks was at once converted into the paramethoxyorthotoluenesulphonic acid at ordinary pressure, and the acid was converted into the sulphonamide through the chloride.

The sulphonamide was then oxidized with potassium permanganate to the sulphinide, $C_6H_4 \begin{subarray}{l} \diagup CO \\ -SO_2 \diagdown NH. \\ \diagdown OCH_3 \end{subarray}$

[1] Lachman : This JOURNAL, 18, 372.

[2] This article and the following one are from the dissertation submitted by the author to the Board of University Studies of the Johns Hopkins University, for the degree of Doctor of Philosophy, June, 1894.

[3] This JOURNAL, 15, 320.

The best conditions were found to be as follows : To use the same amount of sulphonamide and potassium permanganate as given by Parks, and to increase the quantity of water to 2 liters, and to this solution to add from 3 to 5 grams of potassium hydrate.

The time required for the oxidation was about the same, from three to four hours. This treatment increased the yield of the sulphinide to between 25 and 30 per cent. From the filtrate of the sulphinide Parks first obtained potassium chloride, and then the acid potassium salt of paramethoxyorthosulphobenzoic acid, crystallized out, while it was found here that by careful evaporation the acid potassium salt first crystallized out. The salt was identified by analysis.

I. 0.1548 gram of salt lost 0.0098 gram of H_2O.

II. 0.2362 gram of dehydrated salt gave 0.0750 gram of K_2SO_4.

	Calculated for $C_6H_3 {<}^{OCH_3}_{-SO_3K.H_2O} {\atop COOH}$	Found.	
		I.	II.
H_2O	6.25	6.33	....
K (dehydrated)	14.44	....	14.38

The acid potassium salt can also be made by oxidizing with potassium permanganate the potassium salt of paramethoxyorthotoluenesulphonic acid. This was tried as directed by Parks, but as the yield was not as good as through the paramethoxysulphinide, the latter method was adopted. The salt was identified by analysis.

0.2689 gram of salt lost 0.0169 gram of H_2O and gave 0.0810 gram of K_2SO_4.

	Calculated for $C_6H_3 {<}^{OCH}_{-SO_3K.H_2O} {\atop COOH}$	Found.
H_2O	6.25	6.28
K	13.58	13.52

Parks's directions for the conversion of the paramethoxysulphinide and the acid potassium salt of paramethoxyorthosulphobenzoic acid into the free paramethoxyorthosulphobenzoic acid, were followed. The conversion of the acid potassium salt was found to take place as stated by Parks, but the trans-

formation of the paramethoxysulphinide into the acid was found to take place somewhat differently, as will be shown further on.

Conversion of Paramethoxybenzoic Sulphinide into Paramethoxyorthosulphobenzoic Acid.

The sulphinide was placed in a balloon-flask; to it was added a sufficient quantity of water and hydrochloric acid, 8 parts of water to 1 part of concentrated hydrochloric acid by weight. The balloon-flask was connected with an inverted condenser, and the liquid boiled until all the paramethoxybenzoic sulphinide was dissolved. The contents of the flask were then evaporated to crystallization. On cooling, long, white needles crystallized out. These were recrystallized. Thinking this was the acid ammonium salt of paramethoxyorthosulphobenzoic acid, the attempt was made to convert it into the ammonium salt of paramethoxydioxybenzoylbenzenesulphonic acid, $C_6H_2\!\!\begin{cases} OCH_3 \\ -COC_6H_3(OH)_2, \\ SO_2ONH_4 \end{cases}$ by treatment with resorcin, but a sulphonfluorescein was obtained. This indicated that the substance used must have been the free paramethoxyorthosulphobenzoic acid. The same experiment was made with the same and different specimens, with like results in all cases. The melting-point was taken and the crystals melted at $104°$, the melting-point of paramethoxyorthosulphobenzoic acid, thus showing that the free acid instead of the acid ammonium salt, is formed by boiling paramethoxybenzoic sulphinide with water and hydrochloric acid, as directed above. Again, the substance was treated with sodium hydrate, and no odor of ammonia could be detected, nor its presence shown by litmus paper. Other properties of the acid were tested and they agreed with Parks's description of paramethoxyorthosulphobenzoic acid. It melted without decomposition at $104°$, and, on cooling, it quickly solidified, and again melted at the same point. From the solution ammonium chloride was obtained and isolated as a product of the reaction; it was separated from the free acid by crystallization from water and alcohol.

This formation of the acid directly from the sulphinide by boiling with water and hydrochloric acid is not in accordance with that described by Remsen and Linn[1] and others, who in the case of the simple benzoic sulphinide obtained the acid ammonium salt of orthosulphobenzoic acid by the above-mentioned method. The above experiments were performed repeatedly, different specimens of paramethoxysulphinide being used, and in every case the paramethoxyorthosulphobenzoic acid, melting at 104°, was obtained.

Paramethoxyorthosulphobenzoic Acid, $C_6H_3\begin{cases} COOH \\ -SO_2OH(2) \\ OCH_3(3)2\frac{1}{2}H_2O. \end{cases}$
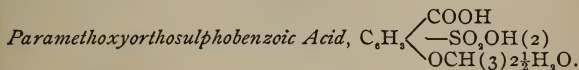
This acid was prepared according to the method just described, from paramethoxybenzoic sulphinide, by boiling with 8 parts of water to 1 part of concentrated hydrochloric acid by weight. It was also prepared from its acid potassium salt, which is formed along with the paramethoxybenzoic sulphinide when paramethoxyorthotoluenesulphonamide is oxidized with potassium permanganate. The acid potassium salt is converted into the acid chloride, $C_6H_3\begin{cases} COCl \\ -SO_2Cl, \\ OCH_3 \end{cases}$ by phosphorus pentachloride, and this by boiling with water into paramethoxyorthosulphobenzoic acid. It is very soluble in water, from which it crystallizes in long, transparent, colorless needles. It melts at 104°, and, on cooling, quickly solidifies, and melts again at the same point on heating. This may be repeated without change in the melting-point.
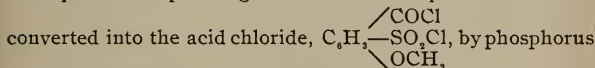
Analyses gave the following results :

I. 0.1698 gram of substance gave 0.0619 gram of H_2O, and 0.2165 gram of CO_2.

II. 0.1758 gram of substance gave 0.0675 gram of H_2O, and 0.2238 gram of CO_2.

III. 0.1691 gram of substance gave 0.1494 gram of $BaSO_4$ (Liebig method).

IV. 0.1633 gram of substance gave 0.1408 gram of $BaSO_4$ (Liebig method).

[1] This JOURNAL, **11**, 73.

	Calculated for $C_6H_3\!-\!\genfrac{}{}{0pt}{}{CO_2H}{SO_3H(2)2\frac{1}{2}H_2O.}{OCH_3(4)}$	I.	II.	III.	IV.
			Found.		
C	34.77	34.77	34.71	....	....
H	4.69	4.05	4.27	....	....
S	11.72	....	....	12.14	11.84

The method of combustion used in these analyses and in those of the sulphonfluoresceïns is that of de Roode.[1]

Acid Potassium Salt, $C_6H_3\!-\!\genfrac{}{}{0pt}{}{CO_2H}{SO_3K.H_2O.}{OCH_3}$—This salt was obtained in the course of preparation of the paramethoxyorthosulphobenzoic acid in several ways as already described. It is very soluble in water, less so in alcohol. Analyses gave the following results:

0.2689 gram of salt lost 0.0169 gram of H_2O and gave 0.081 gram K_2SO_4.

	Calculated for $C_6H_3\!-\!\genfrac{}{}{0pt}{}{CO_2H}{SO_3K.H_2O.}{OCH_3}$	Found.
H_2O	6.25	6.28
K	13.58	13.52

Acid Calcium Salt, $C_6H_3\!-\!\left(\genfrac{}{}{0pt}{}{OCH_3}{SO_2}{CO_2H}\right)_2$ $Ca.4H_2O.$ — This was prepared from the free acid. It is extremely soluble in water. Very slow evaporation is necessary to produce good crystals, and the specimen of the salt analyzed stood over a month before crystals separated that were suitable for analysis.

Analyses gave the following results:

I. 0.0458 gram of salt lost at 135° 0.0058 gram H_2O.
II. 0.0282 gram of salt lost at 135° 0.0035 gram of H_2O.
III. 0.0658 gram of salt gave 0.0138 gram of $CaSO_4$.

	Calculated for $C_6H_3\!-\!\left(\genfrac{}{}{0pt}{}{OCH_3}{SO_2}{CO_2H}\right)_2 Ca.4H_2O.$	I.	II.	III.
			Found.	
H_2O	12.54	12.66	12.41	....
Ca	6.15	....	....	6.17

[1] This JOURNAL, **12**, 236.

Neutral Calcium Salt, $C_6H_3\begin{cases}OCH_3\\SO_3\\CO_2\end{cases}>Ca.1\frac{1}{2}H_2O.$—This is ex-

tremely soluble in water and could not be obtained in good crystals. After filtering and evaporating almost to dryness, fine crystal plates separated out. Analysis gave the following results:

0.042 gram of salt lost 0.0037 gram of H_2O and gave 0.0189 gram of $CaSO_4$.

	Calculated for $C_6H_3\begin{cases}OCH_3\\SO_3\\CO_2\end{cases}>Ca.1\frac{1}{2}H_2O.$	Found.
H_2O	9.09	8.81
Ca	13.46	13.28

Acid Magnesium Salt, $C_6H_3\begin{pmatrix}OCH_3\\SO_3\\CO_2H\end{pmatrix}_2 Mg.3H_2O.$—This is

very soluble in water, but after careful evaporation fine white needles were obtained, which proved to be quite efflorescent.

Analyses gave the following results:

I. 0.0896 gram of the salt lost 0.091 gram of H_2O and gave 0.0176 gram of $MgSO_4$.

II. 0.056 gram of salt gave 0.0125 gram of $HgSO_4$.

	Calculated for $C_6H_3\begin{pmatrix}OCH_3\\SO_3\\CO_2H\end{pmatrix}_2 Mg.3H_2O.$	Found. I.	II.
H_2O	10.00	10.15	....
Mg	4.44	3.93	4.46

Neutral Magnesium Salt, $C_6H_3\begin{cases}OCH_3\\SO_3\\CO_2\end{cases}>Mg.$—It was found

impossible to obtain crystals of this salt, as it is extremely soluble. The solution was evaporated to dryness. Analysis of the residue gave the following results:

0.0151 gram of salt gave 0.0073 gram $MgSO_4$.

	Calculated for $C_6H_3\begin{cases}OCH_3\\SO_3\\CO_2\end{cases}>Mg.$	Found.
Mg	9.45	9.66

Acid Lead Salt, $C_6H_3\diagdown\binom{OCH_3}{\binom{SO_3}{CO_2H}_2}Pb.4\frac{1}{2}H_2O.$—The salt crys-

tallized from concentrated solution in fine white needles. It is very soluble in water, and insoluble in alcohol. Analysis gave the following results:

0.0708 gram of salt at 100° lost 0.0075 gram of H_2O and gave 0.0288 gram of $PbSO_4$.

	Calculated for $C_6H_3\binom{OCH_3}{\binom{SO_3}{CO_2H}_2}Pb.4\frac{1}{2}H_2O.$	Found.
H_2O	10.8	10.59
Pb	27.60	27.79

Neutral Lead Salt, $C_6H_3\diagdown\binom{OCH_3}{\binom{SO_3}{CO_2}}Pb.4H_2O.$—Short, fine,

white needles, very soluble in water. Analysis gave the following results:

I. 0.0667 gram of salt gave 0.0395 gram of $PbSO_4$.

II. 0.0516 gram of salt lost 0.0073 gram of H_2O at 115°, and gave 0.0304 gram of $PbSO_4$.

	Calculated for $C_6H_3\binom{OCH_3}{\binom{SO_3}{CO_2}}Pb.4H_2O.$	Found. I.	Found. II.
H_2O	14.14	....	14.15
Pb	40.66	40.46	40.25

Attempt to Obtain an Anhydride.

About 2 to 3 grams of paramethoxyorthosulphobenzoic acid were placed in a test-tube and gradually heated gently over a free flame and in a sulphuric-acid bath. At 100° it lost its water of crystallization, and at 104° melted. On heating to 145° it again lost water, which condensed on the walls of the tube, and crystals sublimed in the upper part of the vessel. They were fine needles. It was found impossible to get possession of them in sufficient quantity for analysis. Upon higher heating the compound broke down, yielding products which had a most disagreeable, nauseating odor.

Paramethoxysulphonfluorescein.

The first experiment was to introduce 2 molecules of resorcinol into the paramethoxyorthosulphobenzoic acid. Both the resorcinol and the acid were carefully dehydrated and then heated together in the proportion of 1 molecule of acid to 2 molecules of resorcinol. The method of procedure was as follows: The correctly calculated amounts of the dehydrated acid and resorcinol were placed together in a small beaker, which was placed in a sulphuric-acid bath. Suspended from above was a thermometer reaching into the mixture; this could also be used as a stirring rod. Heat was applied very gently and slowly to the bath. At 65° the resorcinol began to melt, and gradually melted until 75° was reached, the mixture becoming wine-red in color. A few crystals of resorcinol sublimed into the upper part of the beaker. The heat was gradually raised until 110°–115° was reached, and the thermometer kept at that temperature as long as the reaction would permit. The reaction went smoothly at that temperature. Stirring must be kept up all the time, as it is necessary for the reaction, otherwise it appears not to take place. When the mixture is stirred, the temperature rises and the source of heat is removed. This same rise of temperature and the necessity of stirring were noted by Blackshear.[1]

After heating for two hours the mass became viscid and reddish-black. It became solid on slight lowering of the temperature, and in some cases it was necessary to raise the temperature in order to keep the mass liquid. On cooling, the fused mass solidified and the surface was glossy with a resinous luster. The cooled mass was then treated with water to dissolve out any unchanged resorcinol or acid and other soluble matter. The fused mass was then dissolved in sodium hydrate, and precipitated with hydrochloric acid, when the sulphonfluorescein comes down as a reddish, granular mass. This was washed thoroughly with hot and cold water by decantation. It was then brought on a filter, and by the aid of a filter-pump washed again. The washing of the sulphonfluorescein is very important. In drying the sub-

[1] This JOURNAL, 14, 455.

stance great difficulties were encountered. When dried on a drying-plate it lost water, as was shown by analysis. Next, drying over sulphuric acid was tried, and in this case also it lost water. The best method was found to be to dry it as thoroughly as possible by the aid of the filter-pump, allow it to stand over night, and then dry it between sheets of drying paper. It then appeared as a brown-red, amorphous mass. This was finely ground for analysis.

The substance was very difficult to burn, and the analytical results indicate that an impure sulphonfluorescein was formed. Different specimens were analyzed several times, but no constant results could be obtained. Analyses gave the following figures:

0.0802 gram of the substance gave 0.1688 gram of CO_2, and 0.0384 gram of H_2O.

	Calculated for $C_{20}H_{16}O_6S$.	Found.
C	57.69	57.15
H	3.87	5.31

Another analysis gave C 59.30 per cent. and H 5.49 per cent.

An analysis for sulphur gave S 6.44 per cent., while the calculated percentage for the above formula is S 7.39 per cent.

The sulphonfluorescein is insoluble in all ordinary solvents; soluble in caustic alkali with a beautiful red-green fluorescence. It is precipitated by hydrochloric acid from its alkaline solution as a red-brown granular mass. In the main the reaction no doubt takes place as represented in this equation:

$$C_6H_3 \diagdown \begin{matrix} CO_2H \\ -SO_2H \\ OCH_3 \end{matrix} + 2C_6H_4(OH)_2 = C_6H_3 \begin{matrix} C[C_6H_3(OH)_2]_2 \\ -SO_2 \\ OCH_3 \end{matrix} \!\!\!\!> O \; +$$

$$2H_2O.$$
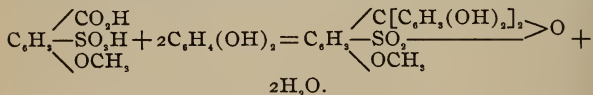
Preparation of the Orcinol Compound.

Orcinol was substituted for resorcinol in the hope of getting a purer product. The method of procedure was the same as in the case of the resorcinol. The orcinol melted at 65°–75°, and reaction began at 110°, water being given off. The temperature in this case had to be raised to 145° in order to com-

plete the reaction, stirring being kept up all the time. The manner of washing, filtering, dissolving, precipitating, and drying was the same as in the case of the resorcinol compound. The yield was about 50 per cent. The orcinol product is a better substance to deal with than the sulphonfluorescein obtained with resorcinol. The same difficulties in drying were also encountered here. In alkaline solution it gives a similar fluorescence, and is precipitated by hydrochloric acid from its alkaline solution.

An analysis was made to determine whether there was water in the compound. The substance was heated at 110°–115° with loss of water, and on raising the temperature no more water was given off.

The analysis gave the following results:

I. 0.0578 gram of substance at 110°–115° lost 0.0024 gram of H_2O.

II. 0.0529 gram of substance gave 0.0271 gram of H_2O, and 0.1140 gram of CO_2.

III. 0.0602 gram of substance gave 0.0312 gram of H_2O, and 0.1314 gram of CO_2.

IV. 0.1076 gram of substance gave 0.0512 gram of $BaSO_4$ (Liebig method).

V. 0.1330 gram of substance gave 0.0634 gram of $BaSO_4$ (Liebig method).

	Calculated for $C_{22}H_{20}O_8S + H_2O$.	I.	II.	Found. III.	IV.	V.
H_2O	3.89	4.15	....	....	....	....
C	57.14	....	58.76	59.07	....	....
H	4.76	....	5.69	5.75	....	....
S	6.92	....	....	....	6.63	6.54

These analyses show that a sulphonfluorescein of the above formula was probably formed, but that it was not pure. It was found impossible to purify it. Blackshear also found it impossible to purify the sulphonfluorescein formed from ortho-sulphonbenzoic acid and resorcinol according to the above method. He prepared it from dioxybenzoylbenzenesulphonic acid.[1]

[1] Sulphonfluorescein has since been prepared in pure condition by treating the chlorides of orthosulphobenzoic acid with resorcinol (Remsen and McKee, this JOURNAL, 18, 802) and by treating the anhydride of the acid with resorcinol (see article by M. D. Sohon in this number).—I. R.

Action of Phenol.—An attempt to introduce two residues of phenol into paramethoxyorthosulphobenzoic acid was tried. The method of procedure was the same as that followed in the case of resorcinol and orcinol. The phenol began to melt at 45° and was all melted at 65°. Slight action began at 85°, and at 105°, on stirring, the thermometer rapidly rose to 130°, indicating reaction, the liquid becoming wine-red in color. The temperature was kept at 115°–120° as nearly as possible; then the temperature was raised to 124°. By continuous stirring the substance gradually became stiff. On cooling, it was treated in the same manner as in case of the resorcinol and orcinol compounds. Precipitated from its solution in sodium hydrate by hydrochloric acid it is a dirty-brown mass with which it was found impossible to deal satisfactorily.

DECOMPOSITION OF PARADIAZOORTHOTOLUENE-SULPHONIC ACID WITH ABSOLUTE METHYL ALCOHOL IN THE PRESENCE OF CERTAIN SUBSTANCES.

By P. R. Moale.[1]

Remsen and Dashiell,[2] working on the decomposition of paradiazoorthotoluenesulphonic acid under different conditions of temperature and pressure, found in the case of ethyl alcohol that both the hydrogen and the ethoxy reactions take place and that high pressure favors the ethoxy reaction and low pressure the hydrogen reaction ; also that the decomposition itself is a function of temperature as well as of pressure, but left open the question as to which influenced the course of the reaction the more. Parks,[3] also working on the decomposition of the above diazo compound with methyl alcohol (absolute), found that the methoxy product only was formed at ordinary, increased, or diminished pressure, namely, paramethoxyorthotoluenesulphonic acid. Beeson[4] found that when diazobenzenesulphate or nitrate is decomposed with sodium methylate or ethylate, the hydrogen reaction takes

place. At the suggestion of Professor Remsen, the decomposition of the above diazo compound with sodium methylate and ethylate was undertaken in the presence of absolute methyl and ethyl alcohols; also the decomposition with absolute methyl alcohol in the presence of ammonia, substituted ammonias, and potassium hydrate.

Decomposition in Presence of Sodium Methylate.

The sodium methylate was made by dissolving a known weight of sodium in a definite volume of absolute methyl alcohol. Knowing the strength of the sodium methylate, the amount necessary for complete reaction with the diazo compound can be readily calculated. To the amount of sodium methylate required for 10 grams of the diazo compound some absolute methyl alcohol was added. The diazo compound was added gradually to the sodium methylate solution. Evolution of nitrogen took place. The temperature was kept down to about 20° during the reaction by a cooling-mixture, as the temperature rises rapidly on addition of the diazo compound. After the calculated amount of diazo compound had been added and nitrogen had ceased coming off, the liquid was evaporated to dryness on the water-bath. It was then finely powdered and treated with a slight excess of phosphorus pentachloride to form the chloride. The chloride was washed and then treated with concentrated ammonia. The product was crystallized from water and was obtained in fine white needles. It melted at 154°, which is the melting-point of orthotoluenesulphonamide. This shows that the hydrogen reaction did take place to some extent. The yield was small, but the reaction is interesting in that it shows that the presence of the alkali tends to cause the hydrogen reaction to take place to some extent, following in the line of Beeson's observations, while Parks found that with the absolute methyl alcohol alone only the methoxy product was formed. The residue left was a black tarry mass with which nothing satisfactory could be done.

Decomposition with Sodium Ethylate.

As before, 19 grams of the diazo compound were used and

the method of decomposition was the same as in case of the sodium methylate. The action was the same as in case of the sodium methylate, though less vigorous. When placed in ice-water the reaction in the beaker stopped. Aldehyde was formed and was detected by its odor. On filtering, a considerable residue was left on the filter. It was a tarry mass from which nothing satisfactory could be obtained. The filtrate was evaporated to dryness. Neither from the residue or filtrate could orthotoluenesulphonamide be obtained. Both the residue and filtrate were reddish-black tarry substances and extremely difficult to work with.

Decomposition of the Diazo Compound with Absolute Ethyl Alcohol in the Presence of Potassium Hydrate.

In this experiment no definite product was obtained. The action was less vigorous than that of the decomposition with sodium methylate or ethylate. The method of procedure was the same as before. After 10 grams of the diazo compound had been added to the calculated weight of potassium hydrate in a sufficient quantity of absolute ethyl alcohol to insure complete decomposition, the contents of the beaker were transferred to a pressure-flask and gently heated. Some decomposition took place at 700 mm. pressure. In about an hour the alcohol boiled quietly, all gas having stopped coming off. The solution was dark-red. On filtering, a black carbonaceous mass was left on the filter. From the filtrate, by evaporation and drying, a reddish mass was obtained which turned to a black gummy mass in the air. Estimations of sulphur and potassium showed that the products were mixtures.

Decomposition of the Diazo Compound with Absolute Methyl Alcohol Saturated with Dry Ammonia Gas.

To the requisite amount of methyl alcohol (absolute) saturated with dry ammonia gas, absolute methyl alcohol was added. To this was gradually added 10 grams of diazo compound. Reaction took place at ordinary temperature. After the reaction was over, the liquid was evaporated to dryness on the water-bath. The substance was finely powdered, and by treatment successively with phosphorus pentachloride and

concentrated ammonia the amide was formed. The amide, after crystallization from water, melted at 164°, which is the melting-point of the amide of paratoluidineorthosulphonic acid, from which acid the diazo compound had been made. For further confirmation the dried product was treated with concentrated hydrochloric acid to convert it into the free acid. The solution was evaporated down on the water-bath and then allowed to crystallize, filtered, and washed well. The acid is insoluble in cold water. Recrystallized from boiling water, it comes down in glistening rhombohedral plates. Analysis gave the following results:

I. 0.0834 gram of substance gave 0.0954 gram of $BaSO_4$ (Liebig method).

II. 0.1106 gram of substance gave 0.1290 gram of $BaSO_4$ (Liebig method).

	Calculated for $C_6H_3{<}^{CH_3}_{SO_3H.H_2O}{>}^{}_{NH_2}$	Found.	
		I.	II.
S	15.61	15.72	16.02

Griffin,[1] working in this laboratory, has shown that in the case of the decomposition of the diazo compound of paratoluidinemetasulphonic acid with absolute methyl alcohol saturated with dry ammonia gas a similar reaction takes place. The course of the transformation is expressed thus:

$$C_6H_3{<}^{CH_3}_{NH_2(4)}{>}^{SO_3H(2)} \;\rightarrow\; C_6H_3{<}^{CH_3}_{N_2}{>}^{SO_3} \;\rightarrow\; C_6H_3{<}^{CH_3}_{NH_2}{>}^{SO_3NH_4} \;\rightarrow$$
$$C_6H_3{<}^{CH_3}_{NH_2(4)}{>}^{SO_3H(2)}.$$
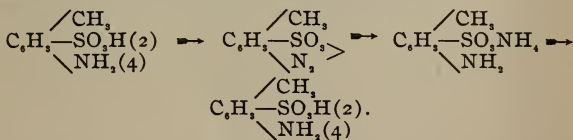
The specimen of the diazo compound used was tested for undiazotized paratoluidineorthosulphonic acid and none was found.

Decomposition with Absolute Methyl Alcohol and Aniline.

Having shown that paradiazoorthotoluenesulphonic acid was converted back to the paratoluidineorthosulphonic acid by absolute methyl alcohol and ammonia, it was thought de-

[1] This JOURNAL, **19**, 171.

sirable to try the action of substituted ammonias, and aniline was used. As before, each specimen of diazo compound was tested for undiazotized acid. In no case was any appreciable quantity of free acid found. In this case three reactions take place, according to the proportions of aniline and methyl alcohol used, one common product and apparently three or four different dye-stuffs being formed. A fourth reaction takes place on gentle heating, with no evolution of gas, a dye-stuff being formed.[1]

PARABENZOYLDIPHENYLSULPHONE

AND RELATED COMPOUNDS.[2]

BY LYMAN C. NEWELL.

Introduction.

The primary object in mind when this research was begun was to make and study orthobenzoyldiphenylsulphone

$$C_6H_4 \Big\langle \begin{matrix} CO.C_6H_5 \\ SO_2.C_6H_5 \end{matrix}$$
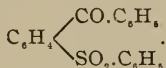
This compound was obtained by Remsen and Saunders[3] by the action of benzene and aluminium chloride on the mixed chlorides and on the symmetrical chloride of orthosulphobenzoic acid. The general plan was to start with toluenesulphone-chloride, $C_6H_4 \Big\langle \begin{matrix} CH_3 \\ SO_2.Cl \end{matrix}$, replace the chlorine by the phenyl group by the Friedel-Crafts reaction, thus passing to tolylphenylsulphone, $C_6H_4 \Big\langle \begin{matrix} CH_3 \\ SO_2.C_6H_5 \end{matrix}$; oxidize the methyl group,

[1] Although Mr. Moale did a good deal of work on these reactions, it was not possible for him to carry the work to completion on account of a lack of time. It was taken up later by Mr. Hollis, and the results reached by him will be published later.—I. R.

[2] From the Author's Dissertation, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen, and carried on under his guidance.

[3] This JOURNAL, **17**, 362.

and thus make phenylsulphonebenzoic acid, $C_6H_4 {\Large <} {\substack{COOH \\ SO_2.C_6H_5}}$;

then treat this acid or its salt with phosphorus pentachloride to

form the corresponding acid chloride, $C_6H_4 {\Large <} {\substack{CO.Cl \\ SO_2.C_6H_5}}$, which,

by the action of benzene and aluminium chloride, would yield

benzoyldiphenylsulphone, $C_6H_4 {\Large <} {\substack{CO.C_6H_5 \\ SO_2.C_6H_5}}$.

It was deemed advisable to begin the work in the *para* series, and, as the results have been so fruitful, nearly the whole investigation has been confined to this series.

Preparation of Material.

The starting-point of this investigation was paratoluene-sulphone chloride. The actual substance used was prepared by the usual method, and was a kilogram of the chloride which had accumulated as a residue in the preparation of the ortho analogue. The raw product was washed with cold water, pumped out on the filter-pump to remove all traces of the liquid ortho chloride, dried, and recrystallized from ether.

Paratolylphenylsulphone.

This compound was made by Michael and Adair,[1] in 1878, from benzenesulphonic acid, toluene and phosphorus pentoxide, and also from toluenesulphonic acid, benzene and phosphorus pentoxide; it was made in the same year by Beckurts and R. Otto[2] by the action of toluene and aluminium chloride on benzenesulphone chloride; and by R. Otto,[3] in 1885, from toluenesulphone chloride, benzene, and mercury diphenyl. The products obtained by these different methods melted at 124°–125°, and were either fine white prisms or small rhombohedral plates.

The method employed in this investigation was analogous to that of Beckurts and R. Otto,[4] the only difference being the use of paratoluenesulphone chloride, which was trans-

1 Ber. d. chem. Ges., 11, 116.   2 *Ibid*, 11, 2068.
3 *Ibid*, 18, 249.   4 *Loc. cit.*

formed into paratolylphenylsulphone by *benzene* and aluminium chloride, *i. e.*, by the Friedel-Crafts reaction. The detailed method is as follows : One part paratoluenesulphone chloride is dissolved in an equal weight of warm benzene, and the solution poured into a flask of convenient size, which is attached to a return-condenser. The flask is then placed in a water-bath, the temperature of the water raised to about 75°, and powdered aluminium chloride introduced into the flask in small portions until an amount has been added which is equal to three-fourths the weight of the benzene used. The reaction proceeds briskly at 75° until the chloride is almost entirely converted into the sulphone. When the evolution of hydrochloric acid has ceased, the temperature is raised to 80°, and kept at this point for three-quarters of an hour. The product of the reaction, which is a black, viscous mass, is poured into a large volume of warm water, acidified with hydrochloric acid and warmed on the water-bath till all the benzene is driven off. The paratolylphenylsulphone then appears on the surface of the water as small brownish-yellow lumps. It is filtered, washed with warm water, purified by animal charcoal, and crystallized from hot, ordinary alcohol. The purified product has the form of hexagonal plates, and melts at 124°-125°. The yield is about ninety-five per cent. of the theoretical amount.

Paraphenylsulphonebenzoic Acid.

This acid was also made by Michael and Adair[1] by oxidizing paratolylphenylsulphone with the calculated amount of potassium permanganate in acetic acid solution, and by boiling the sulphone with potassium permanganate dissolved in a large excess of water. The yield in each case was exceedingly small. The product obtained by both methods crystallized from hot alcohol in fine transparent prisms, which were said to melt above 300°.

The methods employed by Michael and Adair were tried and abandoned, because the yield was small and the methods tedious. The sulphone was also boiled several hours with a mixture of sulphuric acid and potassium dichromate, but this

[1] *Loc. cit.*

method proved unsuccessful. The following method was finally adopted : Five parts of the sulphone are dissolved in the smallest possible quantity of warm glacial acetic acid in a flask which is attached to a return-condenser. The solution is raised nearly to the boiling-point, and 8 parts of chromic acid, also dissolved in the least possible amount of cold glacial acetic acid, are added through the inner tube of the condenser in portions of about 10 cc. each. After each addition of the chromic acid solution, the flask is shaken, the temperature being regulated so that the solution just boils. When all the chromic acid has been added, the mixture is boiled for two hours ; the excess of acetic acid is then distilled off, and when the flask has cooled, the paraphenylsulphonebenzoic acid remains as a fine powder, more or less greenish in color. The contents of the flask are poured into a large porcelain dish and washed several times with hot water. It is better to wash by decantation until only a slight greenish tinge remains, and then wash with the aid of the filter-pump, otherwise a trace of chromium salts will persist in remaining in the crystallized product. The acid is then converted into the sodium salt by boiling with sodium carbonate, and the acid precipitated by hydrochloric acid.

The acid prepared in this way has, when wet, the appearance of whipped cream, and when dry is a pure white powder. It is soluble in boiling nitrobenzene, and separates out as a crystalline mass ; it is soluble in hot glacial acetic acid, from which it crystallizes in small, transparent, double wedge-shaped prisms. Both these solvents are difficult to remove from the crystallized product. It is insoluble in absolute ether and in both hot and cold water. The best solvent is hot alcohol (95 per cent.), from which it crystallizes easily in small, white prisms. Michael and Adair[1] state that the acid melts above 300°. This is incorrect, as several determinations of the melting-point of the crystallized product show conclusively that paraphenylsulphonebenzoic acid melts at 273° uncorr.

Calcium Salt.—Fine white needles separate out of the cooled aqueous solution, which are slightly deliquescent in the air. The following results were obtained on analysis :

[1] *Loc. cit.*

0.2346 gram of the salt heated at 155° to constant weight lost 0.0041 gram of H_2O.

$$\left(C_6H_4\underset{SO_2.C_6H_5}{\overset{COO}{\Big<}}\right)_2 Ca + \tfrac{1}{2}H_2O.$$

	Calculated for	Found.
H_2O	1.58	1.74

0.2305 gram dehydrated salt gave 0.0561 gram $CaSO_4$.

$$\left(C_6H_4\underset{SO_2.C_6H_5}{\overset{COO}{\Big<}}\right)_2 Ca.$$

	Calculated for	Found.
Ca	7.11	7.15

Barium Salt.—This crystallizes from the cooled aqueous solution in fine white needles, which show a marked tendency to arrange themselves in sheaves. Analysis gave the following results :

0.2715 gram air-dried salt when heated at 110° to constant weight lost 0.002 gram H_2O.

$$\left(C_6H_4\underset{SO_2.C_6H_5}{\overset{COO}{\Big<}}\right)_2 Ba + \tfrac{1}{2}H_2O.$$

	Calculated for	Found.
H_2O	0.68	0.73

0.2242 gram dehydrated salt gave 0.0784 gram $BaSO_4$.

$$\left(C_6H_4\underset{SO_2.C_6H_5}{\overset{COO}{\Big<}}\right)_2 Ba.$$

	Calculated for	Found.
Ba	20.81	20.57

Sodium Salt.—This salt crystallizes from alcohol in fine needles, and resembles the barium salt in its tendency to form sheaf-like clusters. It is slightly efflorescent in the air. The following results were obtained on analysis :

0.1711 gram of the salt dried between filter-paper and heated at 110° to constant weight lost 0.0018 gram H_2O.

$$C_6H_4\underset{SO_2.C_6H_5}{\overset{COONa}{\Big<}} + \tfrac{1}{2}H_2O.$$

	Calculated for	Found.
H_2O	1.58	1.05

0.1693 gram dehydrated salt gave 0.0414 gram Na_2SO_4.

$$\begin{array}{ccc} & \text{Calculated for} & \\ & \text{C}_6\text{H}_4\big<\begin{matrix}\text{COONa}\\ \text{SO}_2.\text{C}_6\text{H}_5\end{matrix}\cdot & \text{Found.} \\ \text{Na} & 8.11 & 7.93 \end{array}$$

Paraphenylsulphonebenzoyl Chloride.

This compound can be made by heating paraphenylsul-
phonebenzoic acid or its salts with phosphorus pentachloride.
It is best prepared from the acid. Equal weights of the pow-
dered acid and dry phosphorus pentachloride are intimately
mixed in a flask. To this flask is attached a glass tube about
45 cm. long and having two arms of different lengths bent at
angles of 110° to the horizontal part of the tube; the shorter
arm passes just through the stopper of the flask, while the
longer arm reaches to the bottom of a test-tube surrounded
with ice. The flask is placed in a sulphuric-acid bath,
slowly heated to 200° and kept at this temperature for about
half an hour. If the operation is conducted slowly, this pro-
cess changes all the acid into the corresponding acid chloride,
and most of the phosphorus oxychloride distils over into the
test-tube. Hydrochloric acid is evolved during almost the
whole process. When the operation is over the flask is re-
moved from the bath and allowed to cool. The chloride
solidifies at 145°–150° to a brownish amorphous mass. It is
softened with a little warm water, transferred from the flask to
a mortar, powdered and washed with warm water by decanta-
tion. This operation must be repeated several times, other-
wise the chloride will retain traces of phosphorus oxychloride,
which it is difficult to remove from the crystallized product.
The chloride is carefully dried and crystallized from hot petro-
leum ether (boiling-point 80°–110°). It is not easily soluble
in boiling petroleum ether, but the liquid boiling between
these points was found to be the best of several solvents. The
yield is about 90 per cent. of the theoretical.

The chloride crystallizes from boiling petroleum ether in
fine, glistening, white plates and sometimes in short, white
needles, depending upon the method of extraction and rate
of crystallization. It is soluble in warm, dry benzene, from
which it crystallizes in small rhombohedrons, if the liquid is
slowly evaporated. It is soluble in boiling absolute ether

and crystallizes from this solvent in delicate needles. It is insoluble in petroleum ether boiling between 30° and 50°. The melting-point was found by a Zincke thermometer to be 145.2°–145.8°.

When the chloride is boiled with water the corresponding acid is regenerated and hydrochloric acid is formed. A determinaton of chlorine by this method gave the following result:

0.1697 gram chloride gave 0.0845 gram AgCl.

	Calculated for $C_{13}H_9SO_3Cl$.	Found.
Cl	12.62	12.31

The chlorine was also determined by the following method: The chloride was heated just to the boiling-point for several hours with a dilute solution of caustic potash and then acidified with dilute nitric acid; the regenerated acid is filtered off and the chlorine precipitated as usual. By this method 12.42 per cent. of chlorine was found.

The chloride is slightly volatile. When 0.0505 gram of the air-dried substance was slowly heated to 137° it lost 0.0043 gram. In accordance with the analysis, general conduct, and method of preparation, this chloride has the formula $C_6H_4\Big\langle{}^{CO.Cl}_{SO_2.C_6H_5}$.

Paraphenylsulphonebenzamide.—When paraphenylsulphonebenzoyl chloride is treated with an excess of concentrated ammonium hydroxide at the ordinary temperature, and allowed to stand twenty-four hours with occasional stirring, there is no visible change, since both the chloride and the product of the reaction are insoluble in the liquid used. The white powder which finally settles to the bottom of the beaker has much the same appearance as the chloride, but it is insoluble in boiling petroleum ether (boiling-point 80–110°) and also in hot anhydrous ether. From hot alcohol (95 per cent.) it separates out in small transparent acicular crystals, which melt at 242°–243° (uncorr.).

Analysis for nitrogen by the absolute method and for sulphur by Liebig's method gave the following results:

I. 0.3743 gram substance gave 16.44 cc. = 0.0206 gram nitrogen under standard conditions.

II. 0.3545 gram substance gave 0.3212 gram $BaSO_4$.

	Calculated for $C_{13}H_{11}SO_3N$.	I.	Found. II.
N	5.37	5.55	....
S	12.27	....	12.45

The filtrate from the above method of preparation, when evaporated to dryness, gave nothing but ammonium chloride. The method of preparation together with the analysis show this compound to be the amide corresponding to paraphenyl-

sulphonebenzoyl chloride, $C_6H_4 \begin{cases} CO.NH_2 \\ SO_2.C_6H_5 \end{cases}$.

Paraphenylsulphonebenzanilide.—This anilide is best made in the following manner : Paraphenylsulphonebenzoyl chloride is dissolved in warm dry benzene contained in an Erlenmeyer flask, and an excess of aniline added, drop by drop, with constant shaking. When all the aniline has been added and the mixture shaken for about ten minutes, cold water is added to dissolve the aniline hydrochloride. At this stage the aniline appears as a white gummy mass floating on the surface of the liquid. The mixture is filtered and the anilide washed with warm benzene and finally with cold alcohol. The filtrate, on evaporation to dryness, proved to contain nothing but aniline hydrochloride.

The anilide is soluble in hot alcohol (95 per cent.), but insoluble in boiling petroleum ether (boiling-point 80°–110°), in hot absolute alcohol, boiling caustic soda, and boiling hydrochloric acid. It crystallizes from alcohol in transparent small prisms which melt at 202°–203° (uncorr.).

Analyses made by the same methods as in the case of the amide (*supra*) gave the following results :

I. 0.2904 gram substance gave 10.43 cc. = 0.01308 gram nitrogen under standard conditions.

II. 0.3073 gram substance gave 0.213 gram $BaSO_4$.

	Calculated for $C_{19}H_{15}SO_3N$.	I.	Found. II.
N	4.16	4.50	....
S	9.48	....	9.52

The method of preparation and analysis show that this compound is the anilide of paraphenylsulphonebenzoic acid, and hence has the formula $C_6H_4 \Big\langle \begin{array}{l} CO.NHC_6H_5 \\ SO_2.C_6H_5 \end{array}$

Parabenzoyldiphenylsulphone.

The detailed method used in the preparation of this compound is as follows : Ten grams of the chloride is dissolved in twice its weight of warm benzene in a small beaker. When the temperature is 70°–75°, from 12 to 15 grams of powdered aluminium chloride is added in three portions ; if the action is too vigorous the liquid is allowed to cool below 70°, when the reaction almost ceases. As the operation proceeds, hydrochloric acid is evolved and the product of the reaction settles to the bottom of the beaker as a dark-red oily liquid. The transformation is complete when no more hydrochloric acid is evolved on raising the temperature to the boiling-point of the benzene, the whole operation requiring not more than fifteen minutes. The contents of the vessel were poured into a large volume of water and acidified with hydrochloric acid. The reddish oil solidified to a yellowish-brown, flocculent mass, which encrusted the surface of the liquid after the last traces of benzene had been driven off on the water-bath. It was then washed free from acid with warm water, and crystallized from alcohol (95 per cent.), the yield being about 90 per cent.

The substance crystallizes from alcohol in fine, white, lustrous needles, which, when dry, pack together like felt. They require only one purification with animal charcoal, and, when pure, melt sharply at 133° (uncorr.). They are slightly soluble in cold and warm benzene, in warm ether, and very soluble in warm alcohol. They dissolve in warm concentrated nitric acid and in cold, concentrated sulphuric acid, and are recovered unchanged from both. They are not attacked by alcoholic potash even when the substances are boiled together for a day ; and they are stable in the air.

The following results were obtained on analysis :

I. 0.1504 gram gave 0.3851 gram CO_2, and 0.6375 gram H_2O.

II. 0.2257 gram gave 0.1524 gram $BaSO_4$.

III. 0.1310 gram gave 0.0908 gram $BaSO_4$.

IV. 0.2797 gram gave 0.2088 gram $BaSO_4$.

	Calculated for $C_{19}H_{14}SO_3$.	I.	Found. II.	III.	IV.
C	70.78	70.37	....	....	....
H	4.35	4.70	....	....	....
S	9.95	....	9.37	9.53	10.26

The determinations of carbon and hydrogen were made by de Roode's modification of the lead chromate method; the first two determinations of sulphur were made by Liebig's method, and the last by the method of Carius.

When orthobenzoyldiphenylsulphone is heated slowly with an excess of caustic potash " the action takes place rapidly at 200°–210°, with formation of a yellowish-brown mass. This, when warmed with water, partially dissolves; the residue when separated by filtration and recrystallization from alcohol, gives the characteristic rhombic crystals of diphenylsulphone, melting at 123°–124°, and having the solubility and general properties of that compound. The filtrate treated with hydrochloric acid gives a precipitate of benzoic acid."[1]

When parabenzoyldiphenylsulphone is subjected to the same treatment, the results are entirely different. The sulphone was fused twice in a silver crucible, four times in a sealed hard-glass tube, and once in a distilling-bulb. In all cases the general character of the reaction is the same. Incipient fusion produces a greenish scum on the surface of the molten potash, and at the same time a volatile substance is given off having a pleasant ethereal odor.[2] Attempts were made to obtain the substance giving this odor but they were unsuccessful. When the temperature reaches about 200°–210°, the greenish scum turns to a yellowish-brown porous mass, which still remains on the surface of the potash. When the fused mass is treated as in the fusion of the ortho compound, there are no traces of either diphenylsulphone or ben-

[1] Remsen and Saunders, *Loc. cit.*

[2] This volatilization may be an explanation of the low results obtained in the sulphur determinations by Liebig's method.

zoic acid. A variety of results were obtained, even when the fusion was apparently conducted in precisely the same manner. In one instance a substance was obtained which had some properties characteristic of benzoic acid, but it was impure and the quantity was so small that it could not be regarded as a real product of the reaction. In two instances a substance was obtained melting at 126°-128° and crystallizing from hot alcohol (95 per cent.) in small transparent flakes, but the amount was too small for identification. In several of the fusions—especially those performed in the sealed glass tube—a white powder was obtained from an alcoholic solution of that portion of the fused mass insoluble in water. This powder melted at about 90°, but was impure and was not further investigated.

In view of these facts it must be concluded that when parabenzoyldiphenylsulphone is fused with caustic potash, it does not decompose into benzoic acid and diphenylsulphone, differing markedly in this respect from the corresponding ortho compound.

Derivatives of Parabenzoyldiphenylsulphone.

The method of preparation, the properties, and analysis of this compound show that it must have the structural formula

$C_6H_4 \begin{cases} CO.C_6H_5 \\ SO_2.C_6H_5 \end{cases}$. This being the fact, we should naturally

expect it to yield a hydrazone with phenylhydrazine, and an oxime, or oximes, with hydroxylamine, owing to the presence of the carbonyl group, CO, in the compound. Both the hydrazone and the oxime were made.

Hydrazone.—When equal quantities of parabenzoyldiphenylsulphone and phenylhydrazine, dissolved in a convenient quantity of alcohol, are boiled on the water-bath with a return-condenser for three days, lemon-yellow, lustrous needles separate out of the cooled alcohol. These needles when washed free from phenylhydrazine and recrystallized from hot alcohol (95 per cent.) melt sharply at 184° (uncorr.). When boiled for a day with concentrated hydrochloric acid, the substance splits up into phenylhydrazine and the origi-

nal substance. The beautiful yellow color is not removed by animal charcoal, and the substance is stable in the air.

Analysis gave the following results:

I. 0.0518 gram gave 0.0288 gram $BaSO_4$.

II. 0.18775 gram gave 0.496 gram CO_2, and 0.0802 gram H_2O.

III. 0.1953 gram gave 0.5191 gram CO_2, and 0.0970 gram H_2O.

IV. 0.1873 gram gave 0.4943 gram CO_2, and 0.0844 gram H_2O.

V. 0.1420 gram gave 8.05 cc. = 0.01009 gram nitrogen under standard conditions.

	Calculated for $C_{25}H_{20}SO_2N_2$.	I.	II.	Found. III.	IV.	V.
S	7.77	7.64	....	....	....	....
C	72.78	....	72.04	72.48	72.00	....
H	4.86	....	4.75	5.52	5.00	....
N	6.83	....	....	....	....	7.11

The sulphur was determined by the method of Carius, the nitrogen by the absolute method, and the carbon and hydrogen by de Roode's modification of the lead chromate method.

The preparation, general conduct, and analysis of this compound show it to be paradiphenylsulphonebenzoylhydrazone. Its structural formula is probably:

$$C_6H_4 \Big\langle \begin{array}{l} SO_2.C_6H_5 \\ \underset{\parallel}{C.C_6H_5} \\ N.NH.C_6H_5 \end{array}$$
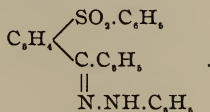
The alcoholic filtrate obtained in the preparation of the first specimens of this hydrazone was evaporated to dryness, and in each case a reddish crystalline mass resulted. This residue was at first thought to be the hydrazone itself. It proved however to be something entirely different. It was soluble in hot water, cold methyl alcohol, hot ordinary ether, and in boiling petroleum ether (boiling-point 80°–110°). Its color when crystallized was a faint yellow and was not removed by animal charcoal. By crystallization from different solvents two kinds of crystals were obtained—small plates and needles

both melting at 125°–127°. Both kinds of crystals were split up into phenylhydrazine and acetic acid in the following manner : The crystals were boiled with concentrated hydrochloric acid for a day, and into this solution, made alkaline with caustic potash, steam was passed ; an oil distilled over with the steam, which had the odor of phenylhydrazine and reduced Fehling's solution. The alkaline liquid into which the steam was passed was evaporated to dryness, and in the residue acetic acid was detected by the ethyl acetate test.

The properties and reactions of this substance—particularly its decomposition into phenylhydrazine and acetic acid—suggested its identity with acetylphenylhydrazine. A sample of pure acetylphenylhydrazine was made according to the method of Fischer.[1] It melted at 128° and had all the properties of the residue mentioned above, including solubility, crystal forms, reducing power, etc. It also was decomposed by the method mentioned above into acetic acid and phenylhydrazine. There seems to be little doubt that the substance in question was acetylphenylhydrazine. The evidence, however, is not conclusive. The substance was not obtained in every instance, in fact only in the first two or three experiments, and then not in very large quantities. Not enough was obtained in a condition pure enough for analysis. While it seems plausible that from some deep-seated cause the alcohol used in the experiment may have been oxidized to acetic acid, and that the acetic acid may have formed acetylphenylhydrazine with the excess of phenylhydrazine present, still the conclusion must be drawn that if acetylphenylhydrazine is formed as a secondary product when parabenzoyldiphenylsulphone is treated with phenylhydrazine in alcoholic solution, it is formed only as the result of some unknown and perhaps accidental cause.

Oxime.—The oxime corresponding to parabenzoyldiphenylsulphone was first made by boiling an alcoholic solution of the sulphone with a slight excess of an aqueous solution of hydroxylamine hydrochloride to which the calculated amount of sodium carbonate had been added. It was found necessary to continue the action for three days in order to transform all

[1] Ann. Chem. (Liebig), **190,** 129.

the sulphone into the oxime. By this method a mixture was obtained which by repeated crystallizations from hot alcohol (95 per cent.) finally yielded thin, irregular leaflets melting at 201° (uncorr.), with evolution of a gas, and small white needles melting at 154° (uncorr.). This method was abandoned for one similar to that used by Auwers[1] for the preparation of the benziloximes. The method finally adopted is as follows: Eleven parts of parabenzoyldiphenylsulphone are dissolved in a slight excess of hot ordinary alcohol, and to this hot solution there is added a clear aqueous solution of 5 parts of hydroxylamine hydrochloride. If the solution is not clear, alcohol is added until the hot solution is perfectly clear. To this solution there is added a filtered aqueous solution of 8 parts of caustic soda. The clear liquid is now boiled for not less than two hours on the water-bath, filtered, if necessary, while hot, and acidified with hydrochloric acid. The oxime which settles out as a white powder is filtered, washed with cold water, dried at 110°, and recrystallized from hot alcohol (95 per cent). The crystals obtained by this method are always the thin, irregular leaflets melting at 201° (uncorr.). When boiled for a day with concentrated hydrochloric acid they split up into hydroxylamine and the original substance. They are insoluble in cold water, and the best crystals come from hot alcohol.

Analysis gave the following results :

I. 0.1986 gram gave 0.4872 gram CO_2, and 0.083 gram H_2O.

II. 0.1987 gram gave 0.4857 gram CO_2, and 0.0809 gram H_2O.

III. 0.1608 gram gave 0.1208 gram $BaSO_4$.

IV. 0.2393 gram gave 8.22 cc. = 0.0103 gram nitrogen under standard conditions.

	Calculated for $C_{18}H_{15}SO_3N$.	I.	II.	III.	IV.
C	67.63	66.92	66.97	....	....
H	4.46	4.64	4.48	....	....
S	9.55	....	....	9.70	....
N	4.16	....	....	....	4.33

The determinations were made by the same methods as in the analysis of the hydrazone.

[1] Ber. d. chem. Ges., **22**, 604.

The preparation, general conduct, and analysis of this compound leave no doubt that it is an oxime of parabenzoyldiphenylsulphone and has one of the two structural formulas represented thus :

$$\underset{\substack{\| \\ \text{N.OH}}}{\overset{\text{I.}}{C_6H_5SO_2.C_6H_4.C.C_6H_5}} \qquad \text{or} \qquad \underset{\substack{\| \\ \text{HO.N}}}{\overset{\text{II.}}{C_6H_5.SO_2.C_6H_4C.C_6H_5}}$$
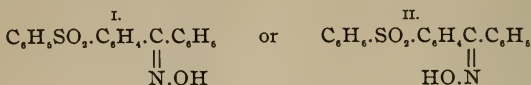
The needles melting at 154° (see above) were obtained only once, and then by the first method of preparation. The conditions under which they were made were reproduced as far as possible, since they were thought to be an isomeric modification of the oxime isolated, but to no avail. The conditions and methods were also modified in various ways, but no trace of an isomer could be obtained after many trials. The work on this possible isomeric form was abandoned on account of lack of material.

The comparative ease with which the oxime and hydrazone of parabenzoyldiphenylsulphone are made, together with the fact that the methods of preparation vary somewhat from those used by Remsen and Saunders in this ineffectual attempt to prepare the oxime and the hydrazone of *ortho*benzoyldiphenylsulphone, suggested the possibility of obtaining a reaction by the methods used in the case of the para compound. Accordingly, some orthobenzoyldiphenylsulphone was purified and recrystallized till it had a constant melting-point (187° uncorr.). It was then boiled with an equal weight of phenylhydrazine in alcoholic solution. At the end of three days the original substance was recovered. At the end of the five days' continuous boiling the orthobenzoyldiphenylsulphone crystallized out of the cooled alcohol. The alcoholic filtrate was evaporated nearly to dryness, and yielded nothing but phenylhydrazine.

Another portion of the orthosulphone was boiled in alcoholic solution with the proper proportions of hydroxylamine hydrochloride and caustic soda under the same conditions as those used for the preparation of the oxime of the parasulphone. At the end of two hours' boiling the original sub-

stance settled out; the action was continued for nine and a half hours and at the end of that time the orthobenzoyldiphenylsulphone crystallized out of the solution when cooled. It had the same crystal form and the same melting-point as the original substance used. These experiments confirm the work of Remsen and Saunders, who obtained neither the oxime nor the hydrazone.

Summary.

The results of this investigation may be briefly summarized as follows:

1. Paratoluenesulphone chloride, by means of the Friedel-Crafts reaction, passes easily into paratolylphenylsulphone.

2. This sulphone can best be oxidized by chromic acid to paraphenylsulphonebenzoic acid, which forms well characterized salts.

3. When heated to 200° (under proper conditions) with phosphorus pentachloride, this acid forms an acid chloride having the formula

$$C_6H_4 \Big\langle {}^{CO.Cl}_{SO_2.C_6H_5}.$$
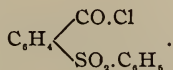
4. Paraphenylsulphonebenzoyl chloride when treated with concentrated ammonium hydroxide at the ordinary temperature, forms an amide having the constitution

$$C_6H_4 \Big\langle {}^{CO.NH_2}_{SO_2.C_6H_5}.$$
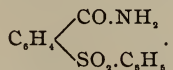
And when treated with an excess of aniline in benzene solution, it yields an anilide of the formula

$$C_6H_4 \Big\langle {}^{CO.NHC_6H_5}_{SO_2.C_6H_5}.$$
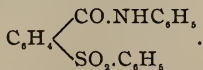
5. A third compound was obtained from paraphenylsulphonebenzoyl chloride, by means of the Friedel-Crafts reaction, which proved to be parabenzoyldiphenylsulphone, a compound analogous to the compound obtained by Remsen and Saunders

from the chlorides of orthosulphobenzoic acid by the same reaction. It has the constitutional formula

$$C_6H_4\Big\langle{}^{CO.C_6H_5}_{SO_2.C_6H_5}.$$
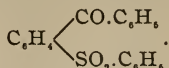
6. This compound, unlike the corresponding ortho compound, is not decomposed into benzoic acid and diphenylsulphone when fused with caustic potash. On the other hand, it does yield a hydrazone and an oxime.

THE ACTION OF ETHYLIC OXALATE ON CAMPHOR (III).

By J. Bishop Tingle.

THEORETICAL.

In the previous papers[1] the preparation of camphoroxalic acid was described, and the formation by it of an additive compound with hydroxylamine, a fact which is not in harmony with the keto formula, $C_8H_{14}\Big\langle{}^{CH.CO.CO.OH}_{CO}$, but is easily explicable if the substance is regarded as an unsaturated hydroxy-derivative, $C_8H_{14}\Big\langle{}^{C:C.OH.CO.OH}_{CO}$. Subsequently C. Harries and F. Lehmann[2] have shown that hydroxylamine and phorone interact in a similar manner; in fact, the reaction appears to be a general one for unsaturated ketones, RCH : CH.COR, to which class camphoroxalic acid belongs. The work described in the following pages was undertaken in the hope of throwing further light on the subject. By the action of acetic anhydride on camphoroxalic acid, three substances are formed melting at 242°, 190°, and 118°, respectively. The yields in all cases were poor, in spite of numerous alterations in the experimental conditions. At present it is impossible to say anything as to the nature of the first compound (m. p. 242°); the second (m. p. 190°) is

[1] This JOURNAL, 19, (1897) 393; J. Chem. Soc., 57, (1890) 652.
[2] Ber. d. chem. Ges., 30, 231, 2726.

probably an anhydride, as it is formed by the action of benzoyl chloride on camphoroxalic acid. The third compound (m. p. 118°) proved to be a monacetyl derivative,

$$C_8H_{14} \left\langle \begin{array}{l} C : C(O.CO.CH_3).CO.OH \\ | \\ CO \end{array} \right. ,$$
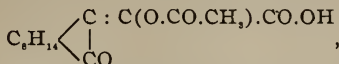
and is also formed by the action of acetic anhydride on ethylic camphoroxalate. The acetyl derivative readily combines with bromine vapor; the product is oily, quickly evolves hydrogen bromide at the ordinary temperature, and the residue could not be induced to crystallize. By the action of bromine vapor on camphoroxalic acid an oily compound is obtained, which crystallizes with difficulty, and could not be completely freed from oxalic acid. When the acid is treated with bromine in chloroform solution, evolution of hydrogen bromide commences immediately. As the product consisted of an oil it was reduced with magnesium amalgam. The substance thus obtained closely resembles camphoroxalic acid in general properties, but an examination of the crystals shows that it is not identical with this, and it will be more fully investigated subsequently. The action of bromine may take place in two ways, according to whether the initial addition occurs in the side-chain or in the camphor nucleus. In the former case, the additive compound would be represented by the formula

$$C_8H_{14} \left\langle \begin{array}{l} CBr.CBr(OH).CO.OH \\ | \\ CO \end{array} \right. , \text{ and would produce, by the}$$
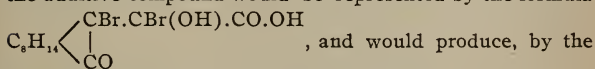
elimination of hydrogen bromide, the compound

$$C_8H_{14} \left\langle \begin{array}{l} C : COBr.CO.OH \\ | \\ CO \end{array} \right. , \quad \text{or} \quad C_8H_{15} \left\langle \begin{array}{l} CBr.CO.CO.OH \\ | \\ CO \end{array} \right. .$$
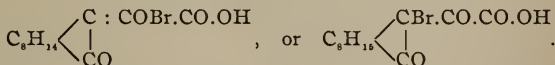
The reduction of the latter compound would then yield a diketonic acid, isomeric with camphoroxalic acid. The fact that the bromo-additive compound gives no coloration with ferric chloride, whilst the substance produced after the elimination of hydrogen bromide does so, supports this view, as does also the readiness with which addition of bromine to camphoroxalic acid takes place. On the other hand it is known that camphor very readily combines with bro-

mine to form a dibromide $C_{10}H_{16}OBr_2$, which easily eliminates hydrogen bromide, and is converted into bromocamphor $C_{10}H_{15}BrO$; this, when reduced, should give, without difficulty, an isomeric camphoroxalic acid, the isomerism being due to a difference in the camphor nucleus. It might be expected too that the negative nature of the carboxyl group would be likely to hinder the addition of bromine to the ethylene linkage in the side-chain. The reduced bromide crystallizes in six-sided plates apparently belonging to the monoclinic system; it melts at $84°$–$84.5°$, and gives a red coloration with ferric chloride; camphoroxalic acid melts at $88°$.

The compound formed by the action of benzoyl chloride on camphoroxalic acid has been referred to above; with benzoic anhydride little or no reaction takes place below $150°$; at this temperature carbonic anhydride is evolved, and no definite product could be isolated.

When quickly distilled under the ordinary pressure, camphoroxalic acid yields some camphor, but a considerable proportion passes over unchanged. Heating with barium hydroxide, in a current of dry purified hydrogen, causes almost complete conversion into camphor and oxalic acid, indicating its hydrolysis at the position of the ethylene linkage. Attempts to convert camphoroxalic acid into an isomeric acid, by prolonged heating at $150°$, were unsuccessful, whilst partial etherification with alcoholic hydrogen chloride failed to show any indication of nonhomogeneity.

When boiled with phenylhydrazine, in anhydrous ether free from alcohol, camphoroxalic acid yields a crystalline salt, which melts and evolves gas at $214°$–$215°$.

By the action of dilute sulphuric acid (1 : 3) on camphoroxalic acid, at $135°$, during three hours, oxalic acid is produced in small quantity, but the larger portion is converted into a new acid, $C_{12}H_{20}O_6$, which crystallizes with some difficulty in granular nodules melting at $92°$–$93°$. It is distinguished from camphoroxalic acid by its sparing solubility in ligroïn, by the production of a deep-blue coloration with alcohol and ferric chloride, and by its failure to yield a sparingly soluble calcium salt. Analysis shows that it is formed by the addition of 2 molecules of water to camphoroxalic acid.

Camphoroxalic acid has been examined crystallographically and belongs to the hexagonal system.

The only specimens of ethylic camphoroxalate hitherto described were mixed with varying quantities of ethylic oxalate; the pure ethylic salt is prepared by heating camphoroxalic acid with highly dilute, absolute alcoholic hydrogen chloride. The compound crystallizes from ligroïn in long needles, aggregated into fern-like patterns, and melts at 40.5°. It is miscible with ether in all proportions, and does not form a copper salt. Its low melting-point has unfortunately hitherto prevented a determination of its crystallographic constants.

The ethylic salt readily combines with dry ammonia, in ethereal solution; the compound is sparingly soluble in the ordinary media, darkens at about 200°, and melts at 225°. With hydroxylamine, at the ordinary temperature, the ethylic salt yields a compound which crystallizes in colorless, slender needles, melting at 120–121°. The yield is poor. With acetic anhydride ethylic camphoroxalate yields, as stated above, acetylcamphoroxalic acid. Bromine acts on ethylic camphoroxalate quite readily, forming first an additive compound, which gradually evolves hydrogen bromide; the final product is oily, and resembles the bromocamphoroxalic acid described above.

Attempts to obtain a benzoyl derivative of ethylic camphoroxalate by Schotten-Baumann's method, or by heating the substances together under varying conditions, were unsuccessful, nor were any better results obtained by the use of benzoic anhydride. These facts indicate that ethylic camphoroxalate is considerably more stable than the free acid, but, with only negative evidence, it would not be justifiable to go beyond this, and regard the ester as possessing a different constitution to that of the acid.

Methylic oxalate reacts with camphor, in presence of sodium, and yields *methylic camphoroxalate*,

$$C_8H_{14} \Big\langle \begin{array}{l} C : COH.CO.OCH_3 \\ | \\ CO \end{array}$$
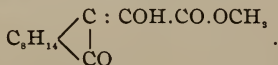
The operation proceeds more slowly than with the homologue, apparently owing to the greatly inferior solubility of the intermediate sodium salt, which covers the sodium wire, and protects it from further action. The product closely resembles the ethylic ester in general properties. The pure compound is obtained by freezing the crude product, or by the etherification of camphoroxalic acid; it crystallizes in long arborescent needles, melts at 74.5°–75°, and is somewhat less readily soluble than the ethylic ester. Examination of the crystals showed that they belonged to the orthorhombic system.

With phenylhydrazine, methylic camphoroxalate yields a

phenylhydrazide, C_8H_{14}
$$\begin{array}{l} C : C.CO.OCH_3 \\ \qquad | \qquad | \\ CO\ NH \\ \qquad\quad | \\ \qquad\quad NH.C_6H_5 \end{array}$$, which crystallizes

in slender colorless, needles melting at 204°–205°. When digested on the water-bath with glacial acetic acid, the phenylhydrazide is converted into *methylic camphylphenylpyrazolecarboxylate*, C_8H_{14}
$$\begin{array}{l} C — C.CO.OCH_3 \\ \ \|\qquad\ \| \\ C\qquad N \\ \ \diagdown\ \diagup \\ \ N.C_6H_5 \end{array}$$, which crystallizes in

colorless needles, and melts at 80.5°–81.5°. The nature of the compound is shown by its giving, when hydrolyzed, the camphylphenylpyrazolecarboxylic acid (m. p. 192°) described in the previous paper.

Isoamylic oxalate, prepared from purified fusel oil, readily combines with camphor in the presence of sodium. The reaction proceeds comparatively rapidly without extraneous heating, and the intermediate sodium compound is readily soluble in ligroïn. A comparison of the behavior of the three homologous oxalates towards camphor shows that the reactivity increases as the mass of the alkyl becomes greater, but this is by no means due to the effect of mass alone, the solubility in ligroïn or ether of the intermediate sodium salts is a most important factor, and this also increases with the mass of the alkyl, and therefore with its content of carbon.

Crude *isoamylic camphoroxalate*, $C_8H_{14}\begin{cases} C:COH.CO.OC_5H_{11} \\ | \\ CO \end{cases}$,

resembles the ethylic compound in general properties; on standing it gradually deposits needle-shaped crystals, which are comparatively sparingly soluble in ether and ligroïn, and melt at 98.5°–99.5°. Measurements indicate that the crystals belong to the triclinic system. A comparison of the crystallographic characters of camphoroxalic acid and of the methylic and isoamylic salts shows that the grade of symmetry of the crystals becomes lower as the molecular weight increases.

With phenylhydrazine, isoamylic camphoroxalate yields a crystalline, sparingly soluble *phenylhydrazide*.

The compound obtained by the interaction of ethylic camphoroxalate and phenylhydrazine, and described in the previous paper, was stated to be either a phenylhydrazone,

$$C_8H_{14}\begin{cases} CH.C.CO.OC_2H_5 \\ | \quad || \\ CO \ N.NH.C_6H_5 \end{cases},$$

or a phenylhydrazide,

$$C_8H_{14}\begin{cases} C:C.CO.OC_2H_5 \\ | \quad | \\ CO \ NH \\ \quad | \\ \quad NH.C_6H_5 \end{cases};$$
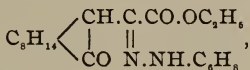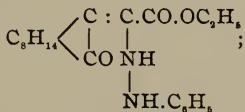
further investigation has shown that it has the latter constitution, as it is readily oxidized by heating with carefully purified mercuric oxide in presence of alcohol; the yield of oxidation-product was very poor.

Camphylphenylpyrazolecarboxylic acid when distilled over barium oxide yields an oily substance which gives Knorr's pyrazoline reaction. It probably contains camphylphenylpyrazole, $C_8H_{14}\begin{cases} C.CH \\ || \quad || \\ C \quad N \\ \diagdown\diagup \\ N.C_6H_5 \end{cases}$. Sodium camphyl-

pyrazolecarboxylate injected into the veins of dogs, is without any marked physiological action. Sodium camphoroxalate,
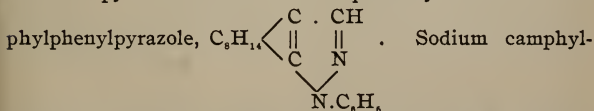
under similar circumstances, is distinctly and rapidly toxic.

Experimental.

Action of Acetic Anhydride on Camphoroxalic Acid.

Camphoroxalic acid (1 molecule) readily dissolves in acetic anhydride (5 molecules) without perceptible evolution of heat ; after boiling with a reflux-condenser for two hours, the liquid is poured into water, neutralized with sodium hydrogen carbonate, and the solid precipitate removed, dried, and recrystallized from a mixture of ether and ligroïn. It is deposited in clusters of colorless, slender needles, darkens at about 240°, and melts at 242°–242.5°. In alcoholic solution it gives no coloration with ferric chloride.

On repeating the experiment with another preparation of acetic anhydride, which, like the first, was from Kahlbaum, none of the above compound was produced, and a portion of the camphoroxalic acid was decomposed. Examination showed that the anhydride was impure ; it was fractionated several times, finally over fused sodium acetate and phosphoric anhydride. A considerable number of experiments were made with this specimen of anhydride under varying conditions of temperature, with and without anhydrous sodium acetate and glacial acetic acid, but the yield of the new compound was always very small, and frequently none was formed. Two other substances were obtained in varying proportions. Both crystallize in colorless, slender needles, the one from ligroïn, the other from a mixture of chloroform and ligroïn ; they melt at 190° and 133.5°–134.5°, respectively, the latter evolving gas. The former compound is insoluble in a solution of sodium hydrogen carbonate, but readily so in ether, and is produced by the action of benzoyl chloride on camphoroxalic acid. The second compound is also obtained by the action of acetic anhydride on ethylic camphoroxalate ; after repeated recrystallization from a mixture of benzene and ligroïn it is deposited in reticulated, stellate, needle-shaped prisms. It is readily soluble in ether, benzene, chloroform, and glacial acetic acid, and is precipitated from the latter on dilution in an amorphous condition ; sodium carbonate solution quickly dissolves it, and it gives no precipitate with cal-

cium chloride in ammoniacal solution.   Analyses gave the
following results :

I. 0.29615 gram substance gave 0.1858 gram H_2O, and
0.6858 gram CO_2.

II. 0.2731 gram substance gave 0.1636 gram H_2O, and
0.63325 gram CO_2.

	Calculated for $C_{12}H_{16}O_4.CO.CH_3$.	Found. I.	II.
C	63.15	63.15	63.23
H	6.76	6.97	6.65

The first analysis was made with a specimen prepared from
camphoroxalic acid ; the second with one from ethylic cam-
phoroxalate.

The compound is therefore *acetylcamphoroxalic acid*,

$$C_8H_{14} \left< \begin{array}{l} C : C(OCO.CH_3).CO.OH \\ | \\ CO \end{array} \right. .$$
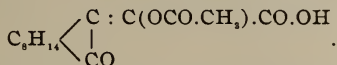
Very many attempts were made to devise a satisfactory
method for the preparation of the compound, but without
much success.   When prepared from camphoroxalic acid,
acetic anhydride alone should be used, and the mixture boiled
in the manner described above ; the product is poured into
water, neutralized with sodium hydrogen carbonate, and ex-
tracted with ether ; the aqueous solution is then treated with
dilute sulphuric acid in excess, and extracted twice or thrice
with ether.   This ethereal solution is dried, the ether re-
moved, and the residue allowed to crystallize spontaneously.
To obtain the acetyl derivative from ethylic camphoroxalate,
the crude ester (1 molecule) is mixed with acetic anhydride
(2 molecules), diluted with three parts glacial acetic acid ;
the solution is heated on the water-bath for fifteen minutes,
then boiled for ten minutes, poured into water, and separated
in the manner just described.

Action of Bromine on Acetylcamphoroxalic Acid.

The acetyl derivative reacts only slowly with bromine in
chloroform solution at the ordinary temperature, but on warm-
ing hydrogen bromide is copiously evolved.   After removal
of the chloroform the residue showed no signs of crystalliza-

tion, and was not further investigated. With bromine vapor at the ordinary temperature the well-dried acetyl derivative speedily reacts, and liquefies; hydrogen bromide is slowly evolved, but no crystalline product could be obtained.

Action of Bromine on Camphoroxalic Acid.

Bromine reacts with the acid more readily than with the acetyl derivative, but the results are similar. In chloroform solution the evolution of hydrogen bromide commences almost immediately after the addition of bromine, and without the application of heat. After removal of the chloroform the oily residue gave, in alcoholic solution, a reddish-green coloration with ferric chloride. In order to eliminate, if possible, any secondary action of hydrogen bromide, the behavior of silver camphoroxalate towards bromine was examined, but only oily products could be obtained. Liquefaction speedily takes place when camphoroxalic acid is exposed to bromine vapor at the ordinary temperature, and hydrogen bromide is slowly evolved; the oil was dissolved in ether, the solution washed with sodium carbonate solution, and the alkaline liquid acidified with dilute sulphuric acid, and extracted with ether. This ethereal solution is reddish-brown, and leaves a similarly colored oily residue when evaporated at the ordinary temperature, but if the ether is distilled off on the water-bath, an almost colorless oil is obtained which, in alcoholic solution, gives no coloration with ferric chloride. After remaining for a week, hard crystalline nodules are deposited, which melt at about 130°, but could not be purified by crystallization. The substance is readily soluble in chloroform or ether at the ordinary temperature, but when the solutions are evaporated spontaneously, or by means of a rapid current of air, oil is always found with the crystals.

The analytical results show that the compound consisted of bromocamphoroxalic acid, $C_{12}H_{15}O_4Br$ (91.7 per cent.), and oxalic acid (8.3 per cent.); the latter could not be removed owing to the difficulties described above. The bromo-acid has well-developed acidic properties, and readily dissolves in sodium carbonate solution with evolution of carbonic anhydride; in alcoholic solution ferric chloride produces a reddish-

brown precipitate. The *silver salt* is colorless and slowly decomposes, silver bromide being produced. The *copper salt* is pale blue, and tolerably readily soluble in water, from which it can be recrystallized ; it melts at about 65°.

When reduced with zinc dust and acetic acid the bromo derivative yields only oily products, but by the action of magnesium amalgam, prepared by H. Fleck's method,[1] at the ordinary temperature, in absolute alcoholic solution, the bromine is easily removed. The resulting product is similar to camphoroxalic acid in general properties, but melts at 84°–84.5° instead of at 88°.

The crystals appear to be monoclinic,[2] and consist of six-sided plates. They are faintly doubly refracting, and, on the large face (001), show the triaxial interference-figure. Optical character +. The axial plane is nearly perpendicular to (001). The plates are generally aggregates, and the angles are not measurable with a reflecting goniometer. With the microscope goniometer the angles of the plates are about 120°.

Action of Barium Hydroxide on Camphoroxalic Acid.

The acid was intimately mixed with the hydroxide in equimolecular proportion, dried at 100°, and distilled in a current of purified, well-dried hydrogen. The distillate had a peculiar, pungent, characteristic odor, but from it only water and camphor could be isolated. The residue also contained a little camphor, together with barium oxalate, showing that the camphoroxalic acid had been hydrolyzed at the position of the double linkage.

Action of Heat on Camphoroxalic Acid.

Attempts to obtain an isomeric compound by heating camphoroxalic acid were unsuccessful. No change is produced in its melting-point by prolonged heating at 150° ; at 190°–200° a little carbonic anhydride is evolved, but the greater portion is unchanged even at the end of six hours. Another portion was heated at 250° until gas evolution ceased,

[1] Ann. Chem. (Liebig), (1892) **276**, 129 ; J. Am. Chem. Soc., **17**, 1895, 789.
[2] I am indebted to Dr. A. P. Brown, of the University of Pennsylvania, for all the crystallographic data in this paper.

and the oily residue was distilled under the ordinary pressure. The product consisted mainly of unchanged acid, together with camphor, showing that a portion of the original acid had been hydrolyzed.

Action of Benzoyl Chloride on Camphoroxalic Acid.

Heat is absorbed when benzoyl chloride (1.5 molecules) is mixed with camphoroxalic acid (1 molecule); when heated the mixture evolves hydrogen chloride and darkens slightly; after fifteen minutes it was poured into water, treated with sodium hydrogen carbonate, and extracted with ether in the manner described in the experiments with acetic anhydride. The alkaline extract yielded, in very small quantity, a compound melting at 192°–193°; it is insoluble in ligroin, sparingly so in alcohol, and readily in chloroform; it gives no coloration, in alcoholic solution, with ferric chloride, and appears to be an anhydride identical with one of the products of the action of acetic anhydride on camphoroxalic acid (see above). From the acid ethereal extract only benzoic acid, and occasionally a little unchanged camphoroxalic acid could be obtained.

Action of Benzoic Anhydride on Camphoroxalic Acid.

No definite product could be obtained by the action of benzoic anhydride on camphoroxalic acid; at about 110° crystals of benzoic acid sublimed, and at 150° carbonic anhydride was evolved; the heating was continued at this temperature until no more gas came off, the residue then poured into water, treated with sodium hydrogen carbonate, and extracted with ether in the manner already described. The alkaline ethereal extract gave only a very small residue, which did not become colored when dissolved in alcohol and treated with ferric chloride. From the acid ethereal extract only benzoic acid could be isolated.

Action of Phenylhydrazine on Camphoroxalic Acid.

The substances, in equimolecular proportions, are separately dissolved in anhydrous ether free from alcohol, the solutions mixed, and heated on the water-bath during two

hours with a reflux-condenser. The yield is good. The product is deposited from alcohol, on the addition of ether, in minute colorless needles which darken at 205°, and melt and evolve gas at 214°–215°. It is readily soluble in alcohol (95 per cent.), sparingly so in ether and ligroïn, and insoluble in water. Phenylhydrazine is regenerated by the action of soda or dilute mineral acids. When boiled with water a gas, apparently nitrogen, is evolved. In alcoholic solution it gives a red coloration with ferric chloride; whilst a dark purple one is produced with concentrated nitric acid. The above reactions indicate that the compound is *phenylhydrazine camphoroxalate.*

Action of Dilute Hydrochloric Acid and of Dilute Sulphuric Acid on Camphoroxalic Acid.

Camphoroxalic acid (5 grams) is heated in a sealed tube during eight hours, at 135°, with concentrated hydrochloric acid (6 cc.), and water (12 cc.); on cooling there is no pressure in the tube, and the contents consist of a slightly colored liquid with a hard, brittle, yellowish-brown, horny solid, covered with white arborescent crystals. This is dried, extracted several times with ligroïn to remove unchanged camphoroxalic acid, and crystallized from benzene once or twice. It is deposited in clusters of colorless needles, melting at 92°–93°. It gives, in alcoholic solution, a deep-blue coloration with ferric chloride. It is readily soluble in chloroform, from which it may be recrystallized by the addition of ligroïn. The compound is sparingly soluble in water, dilute hydrochloric acid, or ligroïn, readily dissolves in soda, ammonia, and sodium carbonate solution at the ordinary temperature. No sparingly soluble salts could be prepared. This property affords a ready means of proving that any specimen is free from oxalic acid or camphoroxalic acid since both these give a white precipitate on the addition of calcium chloride in presence of ammonia. The use of dilute sulphuric acid in place of hydrochloric acid is preferable in some respects, the conditions being: camphoroxalic acid (5 grams), dilute (1 : 3) sulphuric acid (24 cc.), heated at 135°–150°, during seven hours. After the extraction with ligroïn it is sometimes advantageous to dissolve the residue in ex-

cess of baryta water, treat the solution with carbonic anhydride until barium carbonate ceases to be precipitated, filter, acidify, and extract the liquid with ether several times. If the proportion of dilute sulphuric acid is increased to 16 cc. per gram of camphoroxalic acid, the mixture being heated in the manner described above, a portion of the latter is hydrolyzed to oxalic acid and camphor.

Analyses gave the following results :

I. 0.2523 gram substance gave 0.1769 gram H_2O, and 0.5148 gram CO_2.

II. 0.32725 gram substance gave 0.2231 gram H_2O, and 0.66695 gram CO_2.

	Calculated for $C_{12}H_{20}O_8$.	Found. I.	II.
C	55.38	55.64	55.58
H	7.69	7.79	7.57

These results agree with an additive compound of camphoroxalic acid and $2H_2O$. The constitution of the substance has not yet been determined. It may be mentioned in this connection that Bishop, Claisen, and Sinclair[1] describe some ferric salts of formyl camphor which exist only in solution, and vary in color from blue to green ; their composition is expressed by the formulæ $FeRCl_2$ and $FeR_4Cl\left(R=C_8H_{14}\Big\langle\begin{smallmatrix}CHO\\ |\\ CO\end{smallmatrix}\right)$.

The dark-red color produced by mixing ferric chloride with an alcoholic solution of camphoroxalic acid or of ethylic camphoroxalate, does not change when the reagent is added in large excess.

Crystallographic Properties of Camphoroxalic Acid.

The substance crystallizes in short prisms ($10\bar{1}0$) terminated by the basal pinacoid (0001) belonging to the hexagonal system. No other forms were observed, and no axial ratio could be determined. The crystals give the uniaxial interference figure on (0001) ; optical character $+$. They exhibit rotatory polarization; one specimen revolved the plane of polarization 10° to the right for a thickness of 0.65 mm. Some of the hexagonal plates appear to show right and left rotatory polarization in different sectors.

[1] Ann. Chem. (Liebig), (1895) **281**, 343.

Preparation of Pure Ethylic Camphoroxalate.

Camphoroxalic acid (22.4 grams) is dissolved in absolute alcohol (120cc.), containing hydrogen chloride (5.52 grams), and boiled during six hours in a reflux-apparatus. The alcohol is distilled off on the water-bath, the residue poured into water, neutralized with sodium hydrogen carbonate, and extracted twice with ether. The ethereal solution is dried and distilled; the oily residue solidifies after remaining for some time, or more quickly when cooled. The ethereal salt is deposited from ligroïn in fern-like aggregates consisting of long needles, melting at 40.5°. It is miscible with ether in all proportions, and is extremely readily soluble in the ordinary media. No copper salt could be isolated; when mixed, in alcoholic solution, with cupric acetate, or in ethereal solution with ammoniacal cupric acetate, the color changes from blue to green, but on evaporating the liquid only resinous products were deposited.

The yield is 72.3 per cent. of the theoretical, but if the acid recovered from the alkaline aqueous liquid is deducted, the yield is quantitative. The above description of the pure ester shows how closely its properties resemble those of the impure product of which an account was given in the previous papers, and indicates that the specimens of the latter cannot have contained much ethylic oxalate.

Analysis gave the following results :

0.2401 gram substance gave 0.1584 gram H_2O, and 0.5854 gram CO_2.

	Calculated for $C_{14}H_{20}O_4$.	Found.
C	66.66	66.49
H	7.93	7.33

In order to test the question of the homogeneity of camphoroxalic acid, a quantity was etherified to the extent of about 50 per cent.; the remainder proved to be identical with the specimens prepared in the ordinary manner. Measurements of the crystals of ethylic camphoroxalate have not been made, owing to their low melting-point; they tend to loose their individuality soon after they have been prepared.

Action of Ammonia on Ethylic Camphoroxalate.

Carefully dried ammonia produces a white precipitate with ethylic camphoroxalate dissolved in anhydrous ether, free from alcohol. The compound is very sparingly soluble in the ordinary media, and was purified by washing with ether; it darkens at about 200°, and melts at 225°. It gives no coloration with alcohol and ferric chloride, or with concentrated nitric acid, in which it dissolves comparatively slowly. At the ordinary temperature dilute sulphuric acid or soda decomposes it slowly; when heated the action is more rapid, and the components are regenerated. If heated alone, ammonia is evolved, a white sublimate is deposited, and a carbonaceous residue is left.

Action of Hydroxylamine with Ethyl Camphoroxalate.

The ethylic salt (1 molecule) is dissolved in alcohol and mixed with a concentrated aqueous solution of hydroxylamine hydrochloride (3.5 molecules); alcohol is added, if necessary, to obtain a clear solution, which is then rendered faintly alkaline with sodium hydrogen carbonate. A white granular precipitate is gradually formed. After remaining at the ordinary temperature during six days, the liquid is poured into water, acidified with dilute sulphuric acid, and extracted three times with ether. The ethereal solution is dried and distilled, and the residue recrystallized twice from a mixture of toluene and ligroïn; it is deposited in colorless, slender needles, melting at 120°–121°. The compound is readily soluble in caustic soda, more slowly in sodium carbonate solution. It dissolves in dilute sulphuric acid when heated, but crystallizes out on cooling. Water does not dissolve it, but when heated it melts and floats on the surface. The nature of the compound is at present uncertain, possibly it may prove to be an additive compound similar to that formed by camphoroxalic acid, which melts at 146.5°, and was described in the previous paper.

Action of Acetic Anhydride on Ethylic Camphoroxalate.

Ethylic camphoroxalate (1 molecule) is mixed with acetic anhydride (2 molecules), diluted with glacial acetic acid

(3 parts), and the liquid heated on the water-bath during fifteen
minutes, then boiled during ten minutes. The product is
poured into water, and treated in the manner described in the
experiments with acetic anhydride and camphoroxalic acid.
The only product which could be isolated is the acetylcam-
phoroxalic acid (m. p. 133.5°–134.5°) described on page 324.
The yield is rather poor, and numerous variations were made
in the experimental conditions in order to improve it, or to
prepare some other compound, but without success.

Action of Bromine on Ethylic Camphoroxalate.

The behavior of ethylic camphoroxalate towards bromine
resembles that of the free acid ; in chloroform solution the ad-
dition of bromine to the ester is attended with evolution of
heat, but the color of the bromine is only slowly discharged.
When the liquid is heated hydrogen bromide is copiously
evolved. After spontaneous evaporation of the chloroform a
yellowish oil remains which has a characteristic penetrating
odor, and slowly deposits crystals of oxalic acid. By the action
of bromine vapor in the manner described in the experiments
with camphoroxalic acid, an oily compound is formed which
could not be induced to crystallize. Its color is at first red,
but as evolution of hydrogen bromide proceeds it gradually
becomes faintly yellow.

Action of Benzoyl Chloride and of Benzoic Anhydride on Ethylic Camphoroxalate.

All attempts to obtain a benzoyl derivative of ethylic cam-
phoroxalate were unsuccessful ; when treated by Schotten-
Baumann's method benzoic acid was the only product that
could be isolated, and a similar result was obtained by heat-
ing the substances mixed in various proportions, and during
different periods. In every case the ethylic salt was either
recovered unchanged, or it suffered decomposition. The re-
sults were similar when benzoic anhydride was employed in
place of the chloride, although the substances were heated at
150° during four hours. In these circumstances almost all
the ethylic salt was recovered.

The details of the experiments are similar to those given in

the case of camphoroxalic acid and benzoyl chloride or benzoic anhydride.

The greater relative stability of the ethylic salt towards these reagents in comparison with the acid is somewhat striking.

Action of Methylic Oxalate on Camphor.

Camphor (31.5 grams = 1.5 molecules) and methylic oxalate (17.7 grams = 1 molecule) are mixed with ligroïn (500 cc.), which has been carefully dried over sodium, and sodium wire (3.5 grams = 1 atom) is added ; the reaction takes place slowly, and in order to render it approximately complete the ligroïn must be boiled on the water-bath with a reflux-apparatus during two to three hours. Methylic oxalate is only sparingly soluble in ligroïn, and the same applies to the sodium derivative, consequently some metallic sodium is always unattacked, and care is required in treating the product with water. The methylic camphoroxalate is separated from camphoroxalic acid exactly like ethylic camphoroxalate in the manner described in the previous paper. The total yield of acid and methylic salt is 40–45 per cent. of the theoretical, but the relative amounts vary greatly according to the duration of the heating ; if this is prolonged the proportion of acid increases considerably. In one experiment the ratio, ester : acid = 1 : 0.74 , in another, when the heating was continued during nearly five hours, the ratio was 1 : 2.1.

The acid was found to be identical with that obtained by the interaction of ethyl oxalate and camphor.

In general properties methylic camphoroxalate closely resembles the ethylic salt. In alcoholic solution it gives a deep-red coloration with ferric chloride, and occasionally the crude product crystallizes.

Pure methylic camphoroxalate is readily obtained by boiling the acid (22 grams) with methylic alcohol (120 cc.), containing 4.25 per cent. by weight of hydrogen chloride. The heating is continued during six hours, and the product treated in the manner described for the preparation of pure ethylic camphoroxalate. The methylic salt is readily soluble

in alcohol and ether, and crystallizes from ligroïn in long arborescent needles melting at 74.5°–75°.

Analyses gave the following results :

I. 0.2511 gram substance gave 0.1605 gram H_2O, and and 0.60415 gram CO_2.

II. 0.3029 gram substance gave 0.2045 gram H_2O.

	Calculated for $C_{13}H_{18}O_4$.	Found. I.	II.
C	65.54	65.61	....
H	7.56	7.10	7.50

The crystals belong to the orthorhombic system. The faces are somewhat curved or irregular rendering measurements difficult. The forms observed were the pyramid (111), prism (110), and brachypinacoid (010). Angles:

$$110 \wedge 110 = 87°12'$$
$$110 \wedge 111 = 50°44'30''$$
$$110 \wedge 010 = 46°24'$$

Axial ratios ă : b̄ : ċ = 0.9523 : 1 : 0.5649. The extinction observed on (110) and (010) was parallel to ċ.

Action of Phenylhydrazine on Methylic Camphoroxalate.

Methylic camphoroxalate (22.7 grams = 1 molecule) is dissolved in carefully dried ligroïn (250 cc.); phenylhydrazine (10.8 grams = 1.25 molecules) added, and the mixture heated on the water-bath with a reflux-apparatus during two and a half hours. The solid product is separated, well washed with dry ether, and recrystallized twice from methylic alcohol. It forms slender white needles, melts at 204°–205°, is insoluble in ligroïn, very sparingly so in chloroform, benzene, or ether, but dissolves more readily in ethylic or methylic alcohol, and in ethylic acetate. Concentrated nitric acid produces a blue coloration which appears purple by transmitted light ; it gradually changes to brown, and finally becomes light red. Addition of water to the recently prepared nitric acid solution causes the compound to be reprecipitated. Concentrated sulphuric acid produces no coloration at the ordinary temperature even on the addition of a crystal of potassium bichromate ; when heated, gas is evolved. The

compound dissolves in dilute sulphuric acid, and in acetic acid when heated, but is insoluble in hot sodium hydrate solution. It is stable when purified, but the crude substance readily decomposes. Analyses gave the following results:

I. 0.3498 gram substance gave 0.2305 gram H_2O, and 0.88315 gram CO_2.

II. 0.38295 gram substance gave 0.2564 gram H_2O, and 0.9742 gram CO_2.

III. 0.2719 gram substance gave 22 cc. nitrogen at 25.5° and 765 mm.

	Calculated for $C_{19}H_{24}N_2O_3$.	I.	Found. II.	III.
C	69.51	68.86	69.38	....
H	7.31	7.32	7.43	....
N	8.53	....	....	9.08

From its properties, mode of preparation, and analogy with the corresponding compound of ethylic camphoroxalate (see under) the compound is a *phenylhydrazide*,

$$C_6H_{14}\left\langle\begin{array}{l}C : C.CO.OCH_3 \\ | \quad | \\ CO \; NH \\ \quad | \\ \quad NH.C_6H_5\end{array}\right.$$
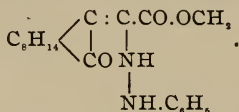
The analysis requires some care, otherwise carbon monoxide is produced, and a portion escapes oxidation.

When mixed with glacial acetic acid, and gently evaporated to dryness on the water-bath, the phenylhydrazide yields *methylic camphylphenylpyrazolecarboxylate*,

$$C_6H_{14}\left\langle\begin{array}{l}C - C.CO.OCH_3 \\ \| \quad\quad \| \\ C \quad\quad N \\ \quad\searrow\swarrow \\ \quad N.C_6H_3\end{array}\right.,$$
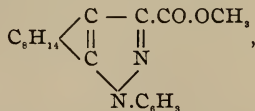
which is deposited from ligroïn in colorless needles, melting at 80.5°–81.5°. The compound was identified by hydrolyzing it with potash; when acidified, the solution precipitates the camphylphenylpyrazolecarboxylic acid described in the previous paper; it melts at 193°–194°, not at 102° as stated there.

Action of Isoamylic Oxalate on Camphor.

The only method mentioned in Beilstein's '' Handbuch'' for the preparation of isoamylic oxalate is one employed by Friedel and Crafts, which consists in heating ethylic oxalate with isoamyl alcohol at 220°–250°; in addition to isoamylic oxalate, ethylic alcohol, diethylic ether, carbon monoxide, and carbon dioxide are produced. Such a method is obviously not well adapted to the preparation of isoamylic oxalate in quantity, consequently it was obtained in the following manner:[1] Isoamylic alcohol (193 grams), obtained by the fractionation of the fusel oil, is mixed with dehydrated oxalic acid (101 grams), and digested on the water-bath during six hours. The upper layer of liquid is removed and fractionated under the ordinary pressure, the portion boiling at 255°–265° being retained ; most of it boiled at 262°—the true boiling-point according to R. Schiff. The yield is 150 grams = 58 per cent. of the theoretical. Isoamylic camphoroxalate is prepared by dissolving camphor (31.5 grams = 1.5 molecules), in anhydrous ligroïn (500 cc.), adding isoamylic oxalate (34.5 grams = 1 molecule), and sodium wire (3.5 grams = 1 atom). The reaction commences vigorously, and proceeds without the aid of heat until about half the sodium is dissolved. The sodium salt is readily soluble in ligroïn. The subsequent operations were performed in the manner described in the previous paper except that the acidified aqueous solution was extracted with ether more frequently, as the isoamylic ester is less soluble than the lower homologues. The yield is 12.5 grams of crude ester and 10.7 grams of crude camphoroxalic acid = 28.4 and 31.8 per cent. of the theoretical, respectively. The ratio, ester : acid = 1 : 1.12. The comparatively large yield of acid is probably due to incomplete separation of the ester from the borneol. This is a matter of some difficulty for the reason stated above. The influence of the various alkyl groups on the reaction is clearly marked ; it proceeds more readily as the molecular weight of the alkyl increases ; whilst this may arise in part from the greater mass, the chief factor influencing the result is undoubtedly the greater solu-

[1] I am indebted to Dr. Fleck, of the University of Pennsylvania, for suggesting the method and for supplying me with specimens of the ester.

bility in ligroïn of the intermediate sodium salt, which increases as the content of carbon rises.

The crude isoamylic ester gives, in alcoholic solution, a red coloration with ferric chloride, and slowly deposits needle-shaped crystals; these are insoluble in benzene or ligroïn, and only sparingly so in chloroform and ether; they melt at $98.5°–99.5°$.

A crystallographic examination showed that the crystals examined were dull, and some of the faces did not give images. Measurements indicate that they are triclinic. The forms measured were assumed as the three pinacoids; a prism which occurred gave no satisfactory image, and therefore the axial ratios of $\breve{a} : \bar{b}$ could not be determined. Angles:

$$001 \wedge 010 = 107°26'$$
$$001 \wedge 100 = 86°$$
$$100 \wedge 010 = 76°36'.$$

This gives by calculation $\alpha = 108° 59' 30''$; $\beta = 81° 22'$; $\gamma = 74° 36'$.

Examined in polarized light the crystals are triaxial and strongly doubly refracting. The index of refraction is moderate.

Isoamylic camphoroxalate readily combines with phenylhydrazine, heat being evolved. The product is very sparingly soluble in the ordinary media; it dissolves in isoamylic alcohol, and is reprecipitated on the addition of ether, but at the temperature of the boiling alcohol a portion of the substance suffers decomposition so that its more complete examination has not yet been made.

Oxidation of Ethylic Camphoroxalate Phenylhydrazide.

The compound produced by the interaction of ethylic camphoroxalate and phenylhydrazine was stated, in the previous paper, to be either a phenylhydrazone,

$$C_8H_{14} \Bigg\langle \begin{matrix} CH \\ | \\ CO \end{matrix} \quad \begin{matrix} . \ C.CO.OC_2H_5 \\ || \\ N \\ | \\ NH.C_6H_5 \end{matrix} \quad ,$$

or a phenylhydrazide,

$$C_8H_{14} \Bigg\langle \begin{matrix} C \\ | \\ CO \end{matrix} \quad \begin{matrix} : \ C.CO.OC_2H_5 \\ | \\ NH \\ | \\ NH.C_6H_5 \end{matrix} \quad .$$
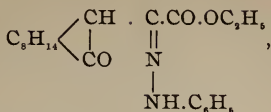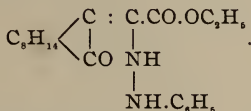
The following experiments show that the latter surmise is correct. Precipitated mercuric oxide, carefully washed free from alkali, and dehydrated by means of absolute alcohol in the manner described by Nef, is added to the phenylhydrazide, suspended in absolute alcohol, and the mixture is heated on the water-bath. Reaction commences immediately, the oxide becomes gray, and more is added as required. When no further change is perceptible the greater portion of the alcohol is distilled off, the residue poured into water, and extracted with ether; after drying the solution and removing the ether, a fluorescent, somewhat tarry residue is obtained which is permeated with crystals. The latter consist partly of unchanged phenylhydrazide, partly of a compound crystallizing in color-less monoclinic plates resembling copper sulphate in shape, and melting at 112.° The quantity of this substance was only small. The purification of the products of the reaction is a matter of considerable difficulty, as decomposition readily takes place.

Action of Barium Oxide on Camphylphenylpyrazolecarboxylic Acid.

The acid (1 molecule) is intimately mixed with barium hydroxide (1.5 molecules), dried at 100° in an atmosphere free from carbon dioxide, mixed with finely-divided iron to increase its conductivity, and distilled under a pressure of about 50 mm. The distillate consists of a yellowish-green oil which showed no tendency to crystallize. It gave a slight reddish-brown color, in alcoholic solution, with ferric chlo-

ride, and a deep reddish-purple one with concentrated nitric acid. It gives Knorr's pyrazoline reaction, and therefore presumably contains camphylphenylpyrazole,

$$C_8H_{14} \left\langle \begin{array}{cc} C & . \ CH \\ \| & \| \\ C & N \end{array} \right. \quad .$$
$$\diagdown N.C_6H_5$$
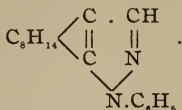
Camphylisoxazole.

Before the preparation of camphylisoxazole, described in the previous paper, the following experiment was performed in order, if possible, to induce the carbonyl group of the camphor molecule to react with hydroxylamine. The hydroxylamine addition-product of camphoroxalic acid was dissolved in glacial acetic acid, hydroxylamine hydrochloride (4 molecules) added, and the mixture heated on the water-bath during six hours. The cold solution deposited crystals resembling those of potassium nitrate in appearance. The product of the reaction was poured into water, neutralized with sodium hydrogen carbonate, made slightly acid with dilute sulphuric acid, and extracted with ether three times. The ethereal solution was dried, and the ether removed ; the residue, after purification, proved to be camphylisoxazole.

Physiological Action of Sodium Camphylphenylpyrazolecarboxylate.[1]

The experiments were made on dogs, the salt being administered in doses of 0.8 gram per kilo of body weight, by intravenous injection of a 5 per cent. solution in "normal saline solution" (containing 0.75 per cent. of sodium chloride). Successive injections were made of 5, 10, and 15 cc. ; immediately following the last injection a slight fall of blood pressure occurred, followed by a gradual rise to normal. A further injection of 5 cc. caused a slight fall in blood pressure, but it rose almost to normal in less than seven minutes. At this stage the reflexes are well given, and the pupil is dilated. A further injection of 5 cc. produced a more pronounced and

[1] I am indebted to Dr. Carter, Professor of Physiology in the University of Texas, for the experimental data on which this description and that of the action of sodium camphoroxalate are based.

steady fall of pressure, accompanied by slight struggling movements; the knee-jerk is absent but the corneal reflex is given well; the pupil is dilated. The respirations became feeble and ceased, the last one taking place about four and a half minutes after the final injection. The temperature two and a half minutes after the last injection was 38.1°, and the blood pressure only a few mm. The following table gives the experimental details: Weight of dog 7.95 kilos. Normal temperature 39.6°.

Time.	Blood pressure in mm.	Pulse beat in ten seconds.	Respiration rate in thirty seconds.	Remarks.
4.56.20	79	28	15	5 cc. injected.
4.57.10	82	28	17	10 cc. injected.
4.58.00	67	27	18	
5.00.10	79	28	27	15 cc. injected.
5.00.30	51	26	27	
5.02.20	51	24	32	
5.03.30	56	23	18	
5.09.00	67	23	15	
5.10.00	73	21	..	Respiration unchanged.
5.15.00	76	29	42	
5.15.30	79	..	..	5 cc. injected.
5.15.50	56	..	..	
5.16.20	56	..	..	Reflexes good, pupil dilated.
5.22.20	67	25	28	5 cc. injected.
5.23.00	38	18	18	Slight struggling.
5.23.20	32	17	..	No knee-jerk, corneal reflex good, pupil dilated.
5.24.00	22	15	30	Respiration very shallow.
5.25.00	13	..	..	Temp. 38.1°.

Physiological Action of Sodium Camphoroxalate.

An experiment was conducted in a similar manner to that with the pyrazolecarboxylate. The salt is rapidly toxic. It was administered by intravenous injection of a 2 per cent. solution in "normal saline"; 3 cc. of this solution, introduced into the jugular vein of a dog, caused almost immediate arrest of respiration and simultaneous fall of blood pressure. Seventy-five seconds after the injection the blood pressure had fallen from 133 mm. to 56 mm., and 2 seconds later the heart collapsed, from this point only beating at irregular intervals

till death took place. It is evident that the salt acts power-fully on the respiratory center, but the rapid fall in blood pressure indicates that death is not entirely due to asphyxia, the vaso-motor center being also paralyzed.

The following table contains a summary of the experimental results :

Weight of dog 7.03 kilos. Two per cent. solution of sodium camphoroxalate, in "normal saline" solution, injected into the jugular vein.

Time.	Blood pressure in mm.	Remarks.
2.46.25	133	
2.46.45		3 cc. injected.
2.47.05	120	Respiration arrested.
2.47.40	56	
2.47.42	16	Heart collapsed. Feeble beats occurred at irregular intervals for about forty seconds.

This investigation is being continued and extended in various directions.

I desire to avail myself of this opportunity of expressing my deep obligations and cordial thanks to Professor Edgar F. Smith, of the University of Pennsylvania, both for his liberality in allowing this investigation to be conducted in the John Harrison Chemical Laboratory, and for his kindly encouragement and advice during its progress.

Lewis Institute, Chicago, Ill.

REVIEWS.

The Arrangement of Atoms in Space. By J. H. van 't Hoff. Second revised and enlarged edition, with a preface by Johannes Wislicenus, Professor of Chemistry at the University of Leipzig, and an appendix on Stereochemistry among Inorganic Substances by Alfred Werner, Professor of Chemistry at the University of Zürich. Translated and edited by Arnold Eiloart. Longmans, Green & Co., London, New York, and Bombay. 1898. viii + 211 pp.

This, as the title-page implies, is a translation of the second edition of van 't Hoff's book of the same title that appeared in 1894, and the latter in turn was a freely revised version of the book that appeared in 1877, when the fundamental theory of stereochemistry was first given to the world in a satisfactory form. It is unnecessary to go into details in discussing this book. The translator has for some time been occupied with

the literature of stereochemistry and has a very thorough knowledge of the subject. He is therefore unusually well qualified for the work of translation, and the work appears to have been well done. Anyone who wishes to consult a book by a master summing up the results obtained in the field of stereochemistry will do well to get this book.

In the Appendix, prepared by Werner, the ideas which were first worked out by him bearing upon the subject of stereochemical isomerism of inorganic compounds are briefly presented—too briefly for the purpose, as without a careful study of a number of examples as presented in Werner's orig-inal articles it is very difficult for anyone to get a clear idea of his theory.   I. R.

Tabellarische Uebersicht der Mineralien nach Ihren Krys-tallographischchemischen Beziehungen Geordnet. Von P. Groth. Vierte Vollständig Neu Bearbeitete Auflage. Brauschweig: Vieweg. 1898. viii + 184 pp.

This admirable book appeals to the chemist more strongly than most books on mineralogy, as it is evident that the author has some appreciation and understanding of the chem-istry of the present time, and he has endeavored in a sensible way to utilize his knowledge for the purpose of simplifying the presentation of the mass of material that the mineralogist has to deal with. While the author's interest in the subject of chemical constitution leads him to raise the question in each group and in connection with each species as to the chemical constitution of the class and of the individual, a cautious chemist will perhaps in some cases be a little surprised to find with what confidence Professor Groth presents the formulas. While a cautious chemist is not likely to be misled by these symbols, a mineralogist without the proper chemical training will be apt to accept them as final and thus be led to assume that more is known regarding the chemistry of the substances represented than is actually the case. On the whole, how-ever, it is better for the mineralogist to accustom himself to these constitutional formulas than to continue to use the old electrochemical formulas that are so commonly used in books on mineralogy.

As regards the changes in the treatment of the subject of the chemical constitution of minerals the author says: "The views upon this subject have been cleared up in many points since the appearance of the third edition in consequence of many new investigations, among which should be promi-nently mentioned the numerous mineral analyses of Penfield and his students as well as the comprehensive theoretical arti-cles by Clarke."   I. R.

PRACTICAL TOXICOLOGY FOR PHYSICIANS AND STUDENTS. By Prof. Dr.
RUDOLF KOBERT. Translated and edited by L. H. FRIEDBURG, Ph.D.
New York : William R. Jenkins. 1897. 201 pp.

This book has come into extensive use in Germany, and
has proved of service in other countries. It, therefore, ap-
pears probable that it will be found of value to American stu-
dents. The translator has used the book with his students
for several years, and is hence perfectly familiar with it. It
is far from pretentious, and is not "intended to compete with
the existing handbooks of toxicology." To use the author's
own words : "The aim of the book shall be reached if it can
be used to advantage by such physicians and students of med-
icine, who are not able to spend much time or much money
upon the study of toxicology."

THE KEKULÉ MONUMENT.

The attention of the readers of this Journal is specially asked
for the circular accompanying this number. It explains itself
fully, and it is hoped that many will respond. There is
scarcely any chemist who has exerted an influence equal to
that exerted by Kekulé upon the advance of chemistry during
the past thirty years. It is difficult to realize how thoroughly
the chemistry of to-day is saturated with his ideas. Not only
do we owe to him the wonderfully fruitful benzene theory, but
we owe to him very largely our present conceptions of the
constitution of chemical compounds—conceptions which, how-
ever imperfect they may be, have been and are of the greatest
service to all chemists, whether they are working with organic
or with inorganic compounds, on problems of constitution or
of dynamics, in the field of pure chemistry or of chemical in-
dustry.

Any subscriptions to the Kekulé fund sent to this Journal
will be acknowledged and forwarded to the General Treasurer
in Germany.   I. R.

Correction.

Vol. **20**, pages 131 and 132 : *For* " Pren" *read* "Preu."

AMERICAN

CHEMICAL JOURNAL

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A DETERMINATION OF THE ATOMIC WEIGHT OF PRASEODYMIUM, AND OF NEODYMIUM.

BY HARRY C. JONES.

The determinations of the atomic weight of the supposed element didymium, have been discussed to a greater or less extent by Meyer and Seubert,[1] Ostwald,[2] and Clarke.[3] Yet, for the sake of completeness and reference, a brief account of what has been done will be given here.

Marignac[4] precipitated the sulphuric acid from a solution 'of didymium sulphate by means of barium chloride, but found that when the precipitate was boiled in the presence of even a large excess of the chloride, it still contained didymium sulphate. His best results were obtained by precipitating the didymium from a solution of the sulphate, as oxalate, by means of oxalic acid, and decomposing the oxalate at a very high temperature, to avoid the presence of superoxide. He found, as the mean of five determinations, 143.58 ($SO_3 = 80$) as the atomic weight of didymium.

Hermann[5] precipitated the didymium from a solution of the sulphate, as oxalate, by means of ammonium oxalate, decom-

1 Atomgewichte, 218. 2 Lehrb. allgem. Chem., 1, 70.
3 A Recalculation of the Atomic Weights, 351–353.
4 Ann. chim. phys. [3], 27, 231 ; 38, 151. 5 J. prakt. Chem., 82, 387.

posed the oxalate by heat, and weighed the oxide. He found 146.7 for the atomic weight of the element. The determination of the chlorine in the chloride gave 142.2 as the atomic weight of didymium. Zschiesche[1] decomposed the sulphate to the oxide, and obtained the value 141.8. Erk,[2] using the method of Hermann, found the atomic weight of didymium to be 142.35. He also precipitated the sulphuric acid from the solution, out of which the didymium had been separated by oxalic acid, as barium sulphate. By this method the atomic weight was found to be 142.29. He employed, in addition, the method which Marignac first used, precipitating the sulphuric acid directly from a hydrochloric acid solution of didymium sulphate, as barium sulphate, and obtained the figure 143.46. This is necessarily erroneous, since, as Marignac has pointed out, some didymium sulphate is always carried down under these conditions.

Hillebrand[3] converted a weighed amount of the metal into the nitrate, and then into the oxide, and found 144.78 (O=16), as the atomic weight of didymium. By the aid of the Bunsen ice calorimeter he found that the specific heat of pure metallic didymium was 0.04563. This number multiplied by 144.78 gives 6.60, which agrees with the law of Dulong and Petit. This shows that the atomic weight of didymium must be expressed by a number very nearly of the order of that given above, and not by two-thirds of this amount. Therefore, didymium forms the normal sesquioxide Di_2O_3, and not DiO.

Cleve[4] heated the oxide in a stream of hydrogen to remove all superoxide, and from the sesquioxide thus obtained he synthesized the sulphate. As a mean of six determinations, he obtained the value 147.01, maximum 147.23, minimum 146.65.

The presence of samarium was later discovered in the above material. This was removed,[5] and ten new syntheses of the sulphate effected from the pure sesquioxide. The mean of these new results is 142.33, maximum 142.49, minimum 142.03.

[1] J. prakt. Chem., **107**, 75.   [2] Ztschr. anal. Chem., **10**, 509.
[3] Ann. der. Phys. Pogg., **158**, 71.   [4] Bull. Soc. Chim., **21**, 246.
[5] *Ibid*, **39**, 289.

Brauner[1] effected the synthesis of the sulphate from the oxide, and as the mean of three determinations obtained the value 146.58.

Later,[2] he made five determinations with samples prepared in different ways, and found as a mean 145.42, with a difference between the highest and lowest value of 0.22. While these results agree fairly well with one another, they differ about a unit from his earlier result, which makes it probable that the oxide first employed contained some element of higher atomic weight. He tested this point as follows:

Some of the didymium oxide used in the first series of experiments, which gave 146.58 as the atomic weight of the element, was fractionally precipitated with ammonia. The atomic weight of didymium, as determined with the fraction which was precipitated last, was found to be 145.40, which made it more probable that the substance first used contained an element with higher atomic weight. Further fractionation confirmed this point beyond question. Brauner concluded that the atomic weight of didymium was probably 145.2 to 145.4.

Bauer[2] synthesized the sulphate from the oxide, and obtained, as a mean of four determinations, the value 142.74.

Auer Von Welsbach[4] showed .that didymium is not an element, but is composed of at least two, thereby invalidating all the preceding results, without, however, affecting the value of the methods which had been used. He effected the separation by fractional crystallization of the double nitrate of ammonium and didymium, from strong nitric acid, and repeating the process several thousand times. The one element forms green salts and green solutions, and the other rose-colored solutions, and the salts are the color of amethyst. To the former he gave the name *praseodymium*, and to the latter *neodymium*. Both the emission and absorption spectra of the two elements are different, but their sum is the same as the corresponding spectrum of didymium.

The elements resemble one another more closely than in

[1] Ber. d. chem. Ges., **15**, 109; Monatsh. Chem., **3**, 14.

[2] Monatsh. Chem., **3**, 499; J. Chem. Soc., **43**, 278.

[3] Inaugural Dissertation, Freiburg, 1884.   [4] Monatsh. Chem., **6**, 477.

any other known cases. Their conduct towards oxygen is, however, very different. Neodymium forms only the sesquioxide Nd_2O_3, while praseodymium forms most readily, the oxide Pr_4O_7; indeed, this is formed whenever the oxalate, or sesquioxide, is heated in contact with air. It is easily reduced to the sesquioxide in a stream of hydrogen gas. Von Welsbach, without giving any details or even the method employed, assigned the atomic weight 143.6 to praseodymium, and 140.8 to neodymium.

Later, Crookes[1] stated that, '' although I have not split up didymium into the two earths, or groups of earths, which are described by Dr. Auer, other processes of fractionation gave me, so to speak, other cleavage planes, or lines of scission through the compound molecule, didymium. * * * * Neodymium and praseodymium must not be considered as actual chemical elements, but only the names given to two groups of molecules, into which the complex molecule didymium splits up, by one particular kind of fractionation.''

The material used in carrying out the piece of work about to be described, was furnished me, with unusual generosity, by Mr. Waldron Shapleigh, of the Welsbach Light Company, Gloucester, New Jersey, who has also made many valuable suggestions in connection with the separation of the elements. I wish to state here, that this work was made possible only by the abundance of the comparatively pure praseodymium and neodymium compounds, which Mr. Shapleigh placed at my disposal.

The Atomic Weight of Praseodymium.

About $1\frac{1}{4}$ kilograms of the double nitrate of praseodymium and ammonium were furnished me by Mr. Shapleigh. It was analyzed spectroscopically by means of the large Rowland spectroscope, with a concave grating of about 21 feet focal length, by Dr. W. J. Humphreys, and found to contain small amounts of neodymium, cerium, and lanthanum. No trace of any of the other rare elements, whose presence might reasonably be expected, could be detected.

The double nitrate, which had been thus far purified, was

[1] Nature, **34**, 266.

treated as follows: The entire mass was dissolved in water containing a little nitric acid, and evaporated until crystals appeared. The solution was then cooled until a part of the double nitrate separated. This was filtered from the solution, and since it contained more of the lanthanum, was discarded. The solution was then strongly acidified with nitric acid, and evaporated on the water-bath until, on cooling, about two-thirds of the total material crystallized out. This was the purest praseodymium, and was used for further crystallization. The mother-liquor was filtered from these crystals and discarded, because it was richest in neodymium. The original substance was thus separated by fractional crystallization into three parts, the first and last being discarded, and the second preserved as the purest material. The second portion was then treated exactly as the original substance, being separated into three portions by fractional crystallization, and the middle portion again treated in the same manner. This process was repeated twenty-one times. Any impurities, such as calcium, iron, etc., were separated from the middle fraction of the last crystallization, by precipitating the praseodymium with oxalic acid, in the presence of nitric acid. Only praseodymium oxalate is thrown down under these conditions. The oxalic acid used, was purified by repeated crystallization from a mixture of alcohol and ether, to remove acid salts, and contained no detectable trace of either potassium or sodium. The water used in dissolving the praseodymium salt, also in washing the oxalate, and in all the processes of crystallization, had been especially purified by distilling, first from acid permanganate, and then from alkaline, in the apparatus described by myself and Mackay.[1] In all of this work the solutions were never allowed to come in contact with glass vessels while warm, but only with porcelain.

The precipitation of the oxalate was effected by pouring very slowly the hot, dilute solution of the double nitrate of praseodymium and ammonium, into a hot, dilute solution of oxalic acid, with vigorous stirring. The oxalate thus pre-

[1] This JOURNAL, 19, 91; Ztschr. phys. Chem., 22, 237.

cipitated, separated in a form which could be easily washed free from impurities. A portion of this oxalate was subjected to spectrum analysis, and was found to contain a trace of neodymium, cerium, and lanthanum. The amount of the neodymium present, was determined by comparing the intensity of the absorption bands of the neodymium in a solution of the praseodymium salt of known concentration, with the absorption bands of the neodymium salt, also of known concentration. A very concentrated solution of the double nitrate of praseodymium and ammonium was prepared, and the intensity of the absorption bands of neodymium noted. Then the solution of the double nitrate of neodymium and ammonium was diluted until the absorption bands were of the same intensity of those of the neodymium in the praseodymium salt. The amount of the neodymium in the solution of the neodymium salt was known, since this was prepared of standard concentration. The amount of the neodymium in the praseodymium salt could thus be calculated directly. By comparing the intensity of the absorption bands of neodymium in the two solutions, by bringing first the one and then the other into the field of the Steinheil spectroscope, we could estimate very closely the amount of the neodymium present in the praseodymium salt. It was found to be 0.06 per cent. and could, therefore, be disregarded.

A further attempt was made to remove the trace of cerium and lanthanum, since the exact amounts present could not be determined accurately, because of the absence of sufficiently intense absorption bands. The oxalate of praseodymium, purified as just described, was decomposed by heat into the oxide, in a platinum vessel. The oxide was dissolved in nitric acid, the excess of acid evaporated, and the solution of the nitrate poured into a large volume of pure boiling water. The cerium present would then be precipitated as the basic nitrate, and a slight cloudiness in the solution was observed. This was repeated until the solution, in a large volume of water, was perfectly clear.

The solution of praseodymium nitrate was evaporated, and enough purified ammonium nitrate added, to form the double salt. The double nitrate was then crystallized from a very

strong nitric acid solution, far stronger than had been hitherto used, in order to remove the remaining trace of lanthanum. This was repeated several times.

The solution of the double nitrate of praseodymium and ammonium, thus purified, was poured into oxalic acid, after being acidulated with nitric acid, as before described, to remove any calcium, iron, etc., which might have gotten in, during the separation of the traces of cerium and lanthanum. The oxalate was washed with the greatest care, converted into the oxide, and this again analyzed spectroscopically by Mr. L. E. Jewell. No trace of cerium was detected, and only a trace of lanthanum.

This oxide, which was used in the following determinations, was blackish-brown, and had the general properties of a superoxide. When dissolved in sulphuric acid there was a copious evolution of oxygen. It was easily reduced to the sesquioxide when heated in a stream of hydrogen gas. When the superoxide was reduced to the sesquioxide it lost 2.5 per cent. of oxygen, corresponding closely to the composition Pr_4O_7, which is the composition of the superoxide described by Von Welsbach.[1] It is thus quite clear that the superoxide of praseodymium which I employed, agreed in all of its essential properties with that isolated and used by Von Welsbach.

The method first employed consisted in dissolving the superoxide in sulphuric acid, evaporating the solution of the sulphate to dryness, and heating it in a platinum vessel, to a temperature above the boiling-point of sulphuric acid. The sulphate was then weighed, dissolved in water to form a very dilute solution, strongly acidified with hydrochloric acid, and the sulphuric acid precipitated by means of barium chloride. It was hoped that by using a very dilute solution, strongly acidified, it would be possible to precipitate all of the sulphuric acid as the barium salt. Several determinations were made, but the results obtained were so discordant as to be entirely valueless. The presence of praseodymium was shown in the precipitate, even after it had been boiled with excess of barium chloride for a considerable time. This fact

[1] Monatsh. Chem., **6**, 489.

had been pointed out by Marignac,[1] but it was hoped that by working in very dilute solutions, which had been strongly acidified, the difficulty could be overcome. It could not, and the method had to be abandoned as entirely useless for the purpose of an atomic weight determination.

The method adopted consisted in reducing the superoxide to the sesquioxide in an atmosphere of hydrogen, and converting the sesquioxide into the sulphate. The details of the process are as follows :

A weighed amount of the superoxide was placed in a porcelain boat, and this within a hard-glass tube, which rested upon a combustion furnace. A stream of hydrogen gas, which had been washed in a solution of sodium plumbate, to remove hydrogen sulphide, and in silver nitrate, to remove arsine, was dried over calcium chloride, and passed through the tube. The superoxide was easily reduced to the sesquioxide on heating. The sesquioxide was allowed to become perfectly cold in the current of hydrogen, and boat and contents were then removed from the tube and weighed. The boat containing the sesquioxide was then returned to the glass tube and reheated in an atmosphere of hydrogen. In no case was there any change in weight caused by the second heating.

A platinum crucible was placed within a ground-glass stoppered weighing-tube, which was then closed and weighed. The sesquioxide was poured from the boat into the crucible, and the whole was reweighed. This gave the weight of the sesquioxide used in a determination.

A considerable excess of sulphuric acid, of medium concentration, was added to the crucible. An equal volume of the sulphuric acid used, was placed in a weighed platinum crucible, evaporated to dryness, and heated exactly as in carrying out a determination, to see whether there was any appreciable residue left behind. In no case did the weight of the crucible increase more than 0.00005 gram, which was therefore negligible. The platinum crucible, containing the oxide and sulphuric acid, was placed in an air-bath constructed of thick sheet copper, and closed at the bottom by a piece of

[1] *Loc. cit.*

very thick sheet copper. The sides of the bath were thickly covered with asbestos paper. The platinum crucible rested upon a porcelain triangle, about an inch from the bottom of the air-bath. Heat was applied to the bath, very gently at first, to avoid all spattering, and then increased, until the solution of the sulphate had evaporated nearly to dryness. Then the bath was heated more strongly, and finally raised to a temperature above the boiling-point of sulphuric acid. The sulphate was maintained at this temperature for some hours, and then weighed. It was reheated and reweighed, and this continued until constant weight was reached. To determine whether only the normal sulphate was present, purified ammonium carbonate was added, and the crucible and contents again heated above the boiling-point of sulphuric acid. There was no change in the weight of the sulphate, showing that only the normal sulphate of praseodymium was present. The sulphate thus prepared was perfectly soluble in water. I was completely unable to verify the observation of Bailey,[1] who stated that '' the sulphate was made into a paste with sulphuric acid and heated at 360°. * * * An approach to a constant weight was manifest, but variations amounting to a milligram or more occurred, and with each successive increase of temperature the loss was accelerated. No range of temperature could be found within which the salt remained perfectly constant.''

I found that the weight of the sulphate remained perfectly constant through a considerable range of temperature, provided the temperature to which it had been heated was sufficient to remove all the excess of sulphuric acid, and decompose any acid sulphate. It is possible that Bailey did not heat the sulphate, or in his case the mixture of praseodymium and neodymium sulphates, to a temperature sufficiently high to leave only the normal sulphate. This is the only way I can account for the result which he obtained.

The crucible containing the sulphate was removed from the air-bath as quickly as possible and placed in the weighing-tube. This was closed and placed in a desiccator over phosphorus pentoxide and allowed to cool. The sulphate was then

[1] J. Chem. Soc., **51**, 676.

weighed in the closed tube, which is necessary, since it absorbs moisture rapidly from the air.

The Results.

	Pr_2O_3.	$Pr_2(SO_4)_3$.	$3(SO_3)$.	$O = 16$ $S = 32.07$ At. wt. Pr.	$O = 15.88$ $S = 31.83$ At. wt. Pr.
1	0.5250	0.9085	0.3835	140.42	139.37
2	0.6436	1.1135	0.4699	140.50	139.45
3	0.7967	1.3788	0.5821	140.38	139.33
4	0.7522	1.3018	0.5496	140.38	139.33
5	0.7788	1.3473	0.5685	140.53	139.48
6	0.6458	1.1172	0.4714	140.54	139.49
7	0.6972	1.2062	0.5090	140.51	139.46
8	0.7204	1.2464	0.5260	140.49	139.44
9	0.8665	1.4990	0.6325	140.54	139.49
10	0.6717	1.1624	0.4907	140.40	139.35
11	0.7439	1.2873	0.5434	140.42	139.37
12	0.6487	1.1224	0.4737	140.47	139.42
	8.4905	14.6908	6.2003	140.46	139.41

The average of the individual determinations is 140.46 when oxygen = 16, or 139.41 when oxygen = 15.88. The difference between the highest and lowest value is 0.16. This series represents all of the determinations which were made, with the exception of two, which were lost by accident and never completed.

The atomic weight of praseodymium, as calculated from the total oxide used, and total sulphate formed, is 140.47 when O = 16, or 139.41 when O = 15.88.

The sesquioxide, prepared by reducing the superoxide in a current of hydrogen, always liberates a small amount of gas when dissolved in sulphuric acid. This is probably occluded hydrogen. The amount of gas thus set free was determined approximately, and found to be so small that it could be disregarded.

The atomic weight of praseodymium, as here determined, may be taken as 140.45 when oxygen = 16, or 139.4 when oxygen = 15.88. This result lays no claim to very great accuracy, because of the apparent impossibility of obtaining an absolutely pure praseodymium compound. However, considering the result of the careful spectroscopic analysis which

was made of the material which I employed, and all the errors which could possibly have entered into the determinations, I see no reason to think that the result can differ from the true atomic weight of praseodymium by more than 0.2 of a unit.

The Atomic Weight of Neodymium.

Somewhat more than 2 kilograms of the double nitrate of neodymium and ammonium were furnished me by Mr. Shapleigh. This was analyzed spectroscopically, and found to contain praseodymium and also a trace of lanthanum. The substance was further purified by fractional crystallization, as described for praseodymium. The entire material was dissolved in water, to which a little nitric acid had been added, and evaporated, until, on cooling, about $\frac{1}{15}$ to $\frac{1}{20}$ crystallized out. A considerable volume of nitric acid was then added, and the larger part of the double salt allowed to separate on further concentrating the solution. The mother-liquor was then carefully filtered from the crystals. The first and third fractions were discarded, and the second preserved for further treatment. The middle fraction was then treated exactly as the original substance had been, was separated into three fractions, and the middle one preserved and again treated in the same manner. This process was repeated twenty-seven times.

The middle fraction of the last crystallization was dissolved in water, strongly acidified with nitric acid, and poured into a dilute solution of oxalic acid, in the same manner as described under praseodymium. This would separate such common impurities as iron, calcium, etc. The oxalate was washed with great thoroughness, dried, and decomposed in a platinum crucible over the blast-lamp. The oxide of neodymium, thus prepared, was again analyzed spectroscopically. It was found to contain praseodymium and a trace of lanthanum. The same method was employed to separate the trace of lanthanum, as in the case of the praseodymium salt.

The praseodymium which remained in the double salt of neodymium, could not be separated by any known method, and must therefore be determined. The amount present was

ascertained with considerable accuracy by studying the intensity of the absorption bands, and comparing these with the absorption bands of the pure praseodymium salt, of known concentration. The exact method is that described under praseodymium. It was found that the double nitrate of neodymium and ammonium contained 1.6 per cent. of the double nitrate of praseodymium and ammonium.

After the lanthanum was separated the neodymium was again precipitated as the oxalate, with oxalic acid, in the presence of nitric acid, by the method already described. The oxalate was converted into the oxide by heating in a platinum crucible over the blast-lamp. The oxide thus obtained was analyzed spectroscopically, special attention being given to the presence of thorium. The only impurity which could be detected was praseodymium, the amount of which had already been determined.

The oxide of neodymium, obtained from the oxalate, does not possess any property of a superoxide as such. It dissolves in sulphuric acid without the evolution of oxygen. When heated in a current of hydrogen exactly as the oxide of praseodymium obtained from the oxalate, it does not change in weight. When hot, the oxide has a marked bluish color, which, however, disappears on cooling. It will thus be seen that the substance which I employed in determining the atomic weight of neodymium, had all the properties described by Von Welsbach,[1] as characteristic of the sesquioxide of neodymium.

The method employed in determining the atomic weight of neodymium was the same, in general, as that used in the case of praseodymium. After it had been found that the oxide obtained from the oxalate did not change in weight when heated in a current of hydrogen, this part of the process was abandoned. The oxide was, however, heated in the platinum crucible just before weighing, and allowed to cool in a desiccator over phosphorus pentoxide, to remove every trace of moisture. The method of synthesizing the sulphate from the oxide, and heating and weighing the sulphate, was the same as employed with praseodymium.

[1] Monatsh. Chem., **6**, 489.

The Results.

	Nd$_2$O$_3$.	Nd$_2$(SO$_4$)$_3$.	3SO$_3$.	$\{ O = 16 \atop S = 32.07 \}$ At. wt. Nd.	$\{ O = 15.88 \atop S = 31.83 \}$ At. wt. Nd.
1	0.8910	1.5296	0.6386	143.58	142.50
2	0.7880	1.3530	0.5650	143.51	142.43
3	0.9034	1.5509	0.6475	143.57	142.49
4	0.7668	1.3166	0.5498	143.51	142.43
5	0.8908	1.5296	0.6388	143.49	142.41
6	0.8848	1.5194	0.6346	143.46	142.38
7	0.8681	1.4903	0.6222	143.57	142.49
8	0.8216	1.4103	0.5887	143.62	142.54
9	0.8531	1.4646	0.6115	143.56	142.48
10	0.8711	1.4957	0.6246	143.50	142.43
11	0.8932	1.5332	0.6400	143.62	142.54
12	0.8893	1.5268	0.6375	143.55	142.47
	10.3212	17.7200	7.3988	143.55	142.47

The average of the 12 determinations is 143.55 when oxygen = 16, or 142.47 when oxygen = 15.88. The difference between the highest and lowest value is 0.16. Three determinations were lost by accident. The atomic weight of neodymium, calculated from the total amount of oxide used, and sulphate formed, is 143.55 when oxygen = 16, or 142.47 when oxygen = 15.88.

The value of the atomic weight of neodymium thus found must be corrected for the presence of praseodymium, which has an atomic weight about 3 units lower. The final value, which, from my work, I should assign to the atomic weight of neodymium, is 143.6 when oxygen = 16, or 142.52 when oxygen = 15.88. I think this value can be regarded as accurate to within about the same limits as indicated in the case of praseodymium.

The oxide of neodymium, prepared as above described, liberated a small amount of gas, presumably air, when dissolved in sulphuric acid. But since this work lays no claim to the last degree of accuracy, due chiefly to the impossibility of effecting complete separations of the rare elements, such corrections were found to be less than the necessary experimental error.

The values which I obtained for the atomic weights of

praseodymium and of neodymium differ widely from those given by Von Welsbach.[1] It is impossible to determine from the paper of Von Welsbach, what he regarded as the atomic weight of oxygen, but since no statement is made, the presumption is in favor of 16. The following comparison will show how widely the two results differ :

	Von Welsbach.	My Results.
Pr	143.6	140.45
Nd	140.8	143.6

There is a discrepancy of about three units in the case of each element. Indeed, if my values were reversed for the two elements, they would not differ widely from those of von Welsbach.

It is not possible to account satisfactorily for the difference between my results and those of Von Welsbach, since the latter has given no details pertaining to his determinations. The fact that if either set of results were interchanged for the two elements, they would agree with the other, suggests that possibly the discrepancy arose in a typographical error in the paper of Von Welsbach, in which his values are recorded as tentative, and in less than a line.

Chemical Laboratory,
Johns Hopkins University,
February, 1898.

VERATRINE AND SOME OF ITS DERIVATIVES.

By George B. Frankforter.

The substance commonly known in pharmacy as veratrine, varies widely in its composition, chemical, physical, and physiological properties. Until recently, it has been exceedingly difficult to obtain different samples with the same general properties. The introduction of the so-called ''Merck veratrine'' has changed matters somewhat, although samples of the Merck alkaloid have been found to vary considerably in their general properties.

One of the chief causes of this exceptional variation, is the extreme difficulty with which the alkaloid crystallizes, thus

[1] Monatsh. Chem., **6,** 490.

almost excluding one of the most important means of purification. Another, and perhaps the most important reason for this wide variation, lies in the fact that almost everyone of the early investigators of the "veratria" has given the name to a different alkaloid or to a mixture of alkaloids.

Pelletier and Caventou[1] first obtained from *Veratrum sabadilla*, an amorphous base which was afterward shown to be a mixture of several alkaloids. For some time, this substance was sold as a medicine under the name "veratria."

Later, Couerbe,[2] in an examination of the sabadilla, obtained three distinct substances. One of these, the most abundant, was amorphous but formed crystallizable salts. He called the base veratrine. Two analyses gave numbers for the formula, $C_{34}H_{42}N_2O_6$.

Merck,[3] in an examination of the same substance, found that when dissolved in very dilute alcohol and allowed to evaporate spontaneously, it crystallized in fine, white, efflorescent needles. His analyses gave numbers for the formula, $C_{64}H_{52}N_2O_{16}$. Several salts were made and analyzed, corresponding well with the above formula.

Schmidt and Köppen[4] obtained from the crude alkaloid, by a method similar to that given by Merck, a crystallizable base which they called veratrine, seven analyses of which gave numbers for the formula, $C_{32}H_{50}NO_9$. These three substances were known and used as veratrine.

Wright and Luff,[5] in a series of experiments on the alkaloids of the *veratra*, have thrown much light on what was hitherto apparently a mass of contradictions. A sharp distinction was made between the several bases which at that time were known as veratrine. They showed that the substance described by Merck was not identical with the veratrine of Couerbe, but that with the exception of a single nitrogen determination, it corresponded well with the base which Schmidt and Köppen had in hand. By a special method of extraction, however, they obtained a substance which corresponded well with Couerbe's veratrine. They

[1] Ann. chim. phys. [II], **14,** 69. [2] *Ibid* [II], **52,** 352.
[3] Ann. Chem. (Liebig), **95,** 200. [4] *Ibid*, **185,** 224.
[5] J. Chem. Soc. (London), **33,** 338.

gave to it the formula, $C_{37}H_{53}NO_{11}$. On saponifying the substance with alcoholic sodium hydroxide, veratric acid and a base which closely resembled cevine were obtained :

$$C_{37}H_{53}NO_{11} + H_2O = C_9H_{10}O_4 + C_{28}H_{45}NO_8.$$
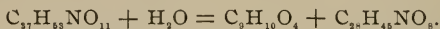
In their examination of crystallized veratrine, Wright and Luff showed that it was entirely different from the above-mentioned veratrine, and that it probably did not exist in an isomeric form. By treating with alcoholic potassium hydroxide, cevadic acid and a new base, cevine, were obtained according to the following reaction :

$$C_{32}H_{49}NO_9 + H_2O = C_5H_8O_2 + C_{27}H_{43}NO_8.$$
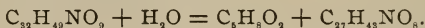
From this reaction crystallized veratrine was called cevadine.

Bossetti,[1] in a discussion of veratrine, found it to exist in the above-mentioned isomeric forms—a crystalline and a non-crystalline. By treating the crystalline form with alcoholic barium hydroxide, angelic acid, and a base of the formula, $C_{27}H_{45}NO_9$, were formed. He called the base cevidine :

$$C_{32}H_{49}NO_9 + H_2O = C_5H_8O_2 + C_{27}H_{43}NO_8.$$
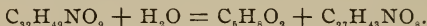
The amorphous form, by the same treatment, yielded veratric acid and veratroine

$$2C_{32}H_{49}NO_9 + 2H_2O = C_9H_{10}O_4 + C_{55}H_{92}N_2O_{16}.$$
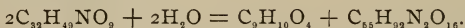
Ahrens,[2] in an examination of crystallized veratrine or cevadine, obtained both cevadic and angelic acids by treating the alkaloid with alkalies. With alcoholic potassium hydroxide, cevadic acid was formed, and with barium hydroxide, angelic acid. Cevadic acid was likewise formed with concentrated hydrochloric acid.

Of special interest is the result of a dry distillation of the alkaloid. At 200° C., a colorless acid was obtained which was identified as tiglic acid. At the same time a base was obtained which was identified as β-picoline. As this experiment is of great importance toward determining the constitution of the alkaloid, it has been repeated. The results obtained are, however, somewhat different.

While a careful comparison of cevadine with the crystal-

[1] Arch. Pharm. (1883), 82.   [2] Ber. d. chem. Ges., **23**, 2700.

lized veratrine has shown them to be identical, and while historically, perhaps, cevadine should take precedence, nevertheless, from the fact that cevadine is the common veratrum alkaloid used at present, it seems advisable to retain the name which associates the alkaloid with the genus of plants from which it is obtained. The name veratrine has, therefore, been retained in the following account of the work.

Experimental Part.

The veratrine with which the following experiments have been made is of a light gray color, and appears, when highly magnified, as imperfect granular crystals. It is slightly soluble in water, very soluble in methyl, ethyl and amyl alcohols, in ether, acetone, chloroform and carbon disulphide. It appears, upon the evaporation of any of these solutions, as a light-brown varnish. On stirring this varnish-like mass with water, it changes to a granular, semicrystalline mass. It refused to crystallize from alcohol. The powdered form has a peculiar bitter, rasping taste, producing a certain numbness of the tongue if taken in very small quantities. This peculiarity readily distinguishes it from any of the other alkaloids. It is a violent sternutatory, producing intense irritation of the nasal mucous membrane. It retards the action of the heart, even when taken in small quantities. It gives a slightly alkaline reaction, which is intensified when the alkaloid is dissolved in alcohol. It gives with dilute nitric acid a pale yellow solution; with concentrated nitric acid, a brown color, and a strong odor of acetic acid. With concentrated sulphuric acid, it produces an orange-red color, which, on standing for some time, becomes fluorescent; with a great excess of acid, it becomes intensely red in transmitted light. With concentrated hydrochloric acid, it immediately produces a blood-red color, which seems to be permanent. It changes, however, to a dark brown color on heating. If the red solution from the hydrochloric acid is rendered slightly alkaline with ammonia, the color changes to a dirty green, even when the alkaloid is present in very small quantities. The melting-point after purification was 146°–148° C.

In order to determine whether or not the substance in hand

was identical with that described by Merck and Ahrens, analyses of the free base, as well as of the gold double salt were made.

No reference was made by the above-named investigators to the water of crystallization. Three determinations were made, the mean of which agreed for one molecule of water.

I. 0.2401 gram of alkaloid, dried at 100°–102°, lost 0.0081 gram H_2O.

II. 0.3108 gram of alkaloid, dried at 100°–102°, lost 0.0103 gram H_2O.

III. 0.5124 gram of alkaloid, dried at 100°–102°, lost 0.0164 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9.H_2O$.	I.	Found. II.	III.
H_2O	3.00	3.33	3.31	3.2

Combustions of the dried substance gave the following :

I. 0.1933 gram gave 0.4572 CO_2, and 0.1441 gram H_2O.
II. 0.2060 gram gave 0.4874 CO_2, and 0.1513 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9$.	I.	Found. II.
C	64.96	64.8	64.53
H	8.29	8.4	8.16

The purity of the alkaloid was further shown by the properties and the melting-point of the gold double salt which melts, according to Merck and Ahrens, at 178°–180°. The recrystallized double salt was found to have the melting-point 178°–182° (uncorr.). The melting-point of the base itself is not given by the above-mentioned investigators. A gold determination gave the following results :

0.2462 gram dried salt gave 0.05171 gram Au.

	Calculated for $C_{32}H_{49}NO_9.HCl.AuCl_3$.	Found.
Au	21.08	21.00

Determination of Methoxyl.

Wright and Luff,[1] in their work on the alkaloids of the sabadilla, stated that cevadine (which is undoubtedly identical with the Merck veratrine) contains one hydroxyl group.

[1] J. Chem. Soc. (London), **33**, 338.

They verified the assumption by the introduction of a ben-zoyl group, forming a monobenzoyl veratrine,

$$C_{32}H_{48}(C_7H_5O)NO_9.$$
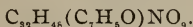
The presence of tiglic acid or methylcrotonic acid was also indicated by its formation when the base was heated with water at 200°. They therefore ascribed to the base the following formula:

$$C_{27}H_{41}NO_6\Big\langle{}^{OH}_{OOC-C(CH_3)=CH-CH_3}.$$
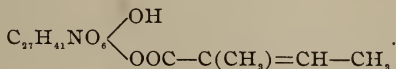
It would appear from this formula that the alkaloid contains no methoxyl group, although no record of such a determination has been given. In order to determine definitely the presence or absence of the methoxyl group, two analyses were made by the Zeisel method with the following results:

I. 0.2461 gram of dried substance gave 0.0698 gram AgI.
II. 0.2021 gram of dried substance gave 0.0636 gram AgI.

	Calculated for $C_{31}H_{46}NO_8(OCH_3)$.	Found. I.	II.
OCH_3	4.19	4.16	4.72

The Iodides of Veratrine.

As stated by Ahrens,[1] veratrine absorbs bromine readily, forming a tetrabromide, $C_{32}H_{49}NO_9Br_4$. It was prepared by triturating veratrine with strong bromine water, when a yellow powder was formed which was purified by filtering and washing with warm water. It proved to be insoluble in water but readily soluble in alcohol, ether, chloroform, and acetone.

On treating the tetrabromide with dilute potassium hydroxide, two bromine atoms were readily removed, a light yellow dibromide, $C_{32}H_{49}NO_9Br_2$, being formed.

Reference is also made by Bauer,[2] to an iodide of veratrine which was prepared by the action of iodine on a salt of veratrine. The formula given is $C_{32}H_{54}N_2O_8HI_3$.

Veratrine Tetraiodide, $C_{32}H_{49}NO_9I_4\cdot 3H_2O$.—A careful examination showed that iodine also combines readily with veratrine forming a series of compounds which in many respects

[1] Ber. d. chem. Ges., **23**, 2700.   [2] Arch. Pharm. [III], **5**, 289.

resemble the bromides. By triturating veratrine with a strong alcoholic solution of iodine, a reddish-brown substance was formed which upon examination appeared to be a mixture of several substances. This was also indicated by the varying melting-point. A great excess of iodine was then added and the substance allowed to stand for several days when a beautiful, light-red, crystalline substance was formed melting at 129°–130°. It is very soluble in methyl and ethyl alcohols forming, upon evaporation, a dark-brown, waxy mass. It is soluble in acetone, forming a wax, which upon standing becomes a dark-red powder. It is insoluble in water, benzol, and ether. By treating with sulphurous acid, the red color disappeared and a light yellow powder was formed which was afterward identified as the monoiodide. With dilute ammonia, the same substance is formed, but with concentrated ammonia, a white, gelatinous substance is formed with some of the properties of the free base. An examination showed it to be different from the free alkaloid, although all of the iodine had been removed.

Great difficulty was experienced in the determination of water of crystallization. It was found, after several determinations, that four hours' drying at 100°–102° was necessary to remove the 3 molecules of water present. It was also found that by drying at 104°–106° some of the iodine was driven off. This explained the difficulty in obtaining satisfactory results in the early analyses. A careful determination of moisture was made, the temperature being gradually raised to 114°, with the following results :

2.362 gram substance dried at 100°   for 2 hours lost 0.082
"   "   "   "   " 100°–102° "   "   "   " 0.118
"   "   "   "   " 100°–102° "   "   "   " 0.119
"   "   "   "   " 100°–104° "   "   "   " 0.152
"   "   "   "   " 100°–104° "   "   "   " 0.179
"   "   "   "   " 100°–105° "   "   "   " 0.190
"   "   "   "   " 100°–105° "   "   "   " 0.224
"   "   "   "   " 100°–105° "   "   "   " 0.224
"   "   "   "   " 102°–106° "   "   "   " 0.240
"   "   "   "   " 102°–106° "   "   "   " 0.247
"   "   "   "   " 104°–107° "   "   "   " 0.276
"   "   "   "   " 104°–107° "   "   "   " 0.299
"   "   "   "   " 105°–108° "   "   "   " 0.327

2.362 gram substance dried at 105°–109° for 2 hours lost 0.341
" " " " " 105°–110° " " " " 0.382
" " " " " 105°–110° " " " " 0.382
" " " " " 110°–112° " " " " 0.389
" " " " " 112°–112° " " " " 0.402
" " " " " 112°–114° " " " " 0.414

The weight appeared to be constant at 110°, even when heated at that temperature for four hours. The substance showed decided indications of decomposition however, at 112°–114°, and at 120° began to frit, changing to an almost black, waxy mass. As will be seen from the above numbers, the substance dried to constant weight at 100° loses 3 molecules of water.

2.362 grams dried at 100° lost 0.118 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9I_4.3H_2O.$	Found.
$3H_2O$	4.68	4.99

It was found, on examination, that the loss which occurred by heating above 102° was due to liberation of iodine, and that by drying at 110° to constant weight, one-fourth of the iodine could be driven off.

2.362 grams substance dried to constant weight at 110° lost 0.382 $I + H_2O$.

	Calculated for $C_{32}H_{49}NO_9I_3 + I + 3H_2O.$	Found.
$I + 3H_2O$	15.7	16.17

An attempt to remove another atom of iodine was unsuccessful, as is indicated by the above experiment, although the loss which occurred between 110°–114° was due to the liberation of iodine.

An analysis of the substance dried at 100° to constant weight was made with the following results:

0.2231 gram of dried iodide gave 0.2834 gram CO_2, and 0.0912 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9I_4.$	Found.
C	34.94	34.64
H	4.45	4.9

Veratrine Triiodide, $C_{32}H_{49}NO_9I_3$.—The red iodide, dried at 110° to constant weight, became a dark-brown, amorphous

powder, which showed no signs of crystallization when treated with water. It is insoluble in ether and much less soluble in methyl and ethyl alcohols than the tetraiodide. It melts at $136°-138°$.

Analyses gave the following results :

I. 0.2034 gram substance gave 0.2938 gram CO_2, and 0.1152 gram H_2O.

II. 0.1945 gram substance gave 0.1405 gram AgI.

	Calculated for $C_{32}H_{49}NO_9I_3$.	I.	II.
C	39.5	39.37	....
H	6.36	6.28	....
I	39.2	....	38.6

While it was evident that more than one-fourth of the iodine could be driven off by drying, repeated attempts to obtain the diiodide were unsuccessful.

Veratrine Monoiodide, $C_{32}H_{49}NO_9I$.—By treating the tetraiodide with dilute ammonia, and allowing to stand for several hours in a warm place, the bright-red color disappeared and a light-yellow granular substance was formed. It proved to be insoluble in water, ether, and chloroform, but very soluble in methyl and ethyl alcohols. A bright-yellow powder is formed on evaporating off the alcohol. It does not form the waxy mass which characterizes the tetraiodide. It was obtained from a dilute alcoholic solution as a fine crystalline powder with a melting-point of $212°-214°$. It contains 2 molecules of water, which were removed by drying at $100°$.

0.3782 gram substance dried at $100°$ lost 0.018 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9I + 2H_2O$.	Found.
$2H_2O$	4.77	4.76

An analysis gave the following :

0.1763 gram dried substance gave 0.0583 gram AgI.

	Calculated for $C_{32}H_{49}NO_9I$.	Found.
I	17.68	17.87

On digesting with strong ammonia for a short time the iodide was completely removed, and a white insoluble gelatinous substance was formed, which at first was regarded as

the free alkaloid. An examination showed that it differed from veratrine in general appearance and solubility. It melted at 189°.

Other Compounds.

Chloralhydroveratrine, $CCl_3CH \begin{cases} O(C_{32}H_{48}NO_8) \\ O(C_{32}H_{48}NO_8) \end{cases}$.—As stated by Wright and Luff,[1] veratrine, heated at 100° with twice its weight of benzoic anhydride, is converted into a monobenzoylveratrine, $C_{32}H_{48}(C_7H_5O)NO_9$. The formation of this compound proved the presence of one hydroxyl group. The writer repeated the experiment in order to determine whether or not more than one hydroxyl group existed in the alkaloid. The impossibility of making more than the mono derivative was sufficient evidence that but one group existed. It was found, however, that this group was so loosely held that it could be replaced by treating with almost any anhydride. Chloral was found to react vigorously on the alkaloid, producing a sort of effervescence. In an excess of chloral the alkaloid dissolves. With a smaller quantity, a waxy mass is formed, which readily changes to a creamy-white, granular powder. This powder was washed thoroughly with ether to remove the free chloral. The substance in the pure state was almost white and crystalline. A determination showed the reaction to be quantitative. Five grams of the veratrine gave 6.1 grams of the pure chloral compound. It is insoluble in ether and chloroform, but very soluble in water and alcohol. It melts at 220°. In its physiological properties, it resembles veratrine. It is a most powerful sternutatory, producing violent irritation of the nasal mucous membrane. In minute quantities it affects the eyes, causing intense pain and contracting the pupils. It is a remarkable local irritant. Applied to the moistened skin, and rubbed, it produces blisters. It is readily decomposed by alkalies. Ammonia decomposes it forming chloral hydrate and veratrine. It is hygroscopic, taking up 2 molecules of water if exposed to the air for some time. The water can readily be removed by drying at 100°.

Analyses gave the following numbers :

[1] J. Chem. Soc., **32**, 351.

I. 0.2394 gram dried substance gave 0.5280 gram CO_2, and 0.1530 gram H_2O.

II. 0.1692 gram dried substance gave 0.0502 gram AgCl.

	Calculated for $CCl_3CH(OC_{32}H_{48}NO_6)_2$	I.	II.
		Found.	
C	60.38	60.2	....
H	7.38	7.1	....
Cl	8.2	....	7.35

The alkaloid formed by the action of ammonia upon the substance was carefully examined in the hope of finding the isomeric base of Schmidt and Köppen. Although the base seemed to have a few different properties from the original veratrine, the gold double salt had exactly the properties and melting-point of the original gold salt.

Veratrine Methyl Iodide, $C_{32}H_{49}NO_9 \cdot CH_3I$.—From the resemblance of veratrine to the alkaloids narcotine and narceine, it was believed that it would form a compound with methyl iodide. It was found, on treating the base with excess of methyl iodide, that the substance readily dissolved with the exception of a very small quantity of gelatinous matter, which proved to be an impurity. By allowing the filtered solution to stand for some hours, or by heating on a water-bath with a reflux condenser, the whole of the base precipitated out as a solid, yellow, crystalline mass. The reaction was completed at the end of an hour on the water-bath, but it required several days at the ordinary temperature to convert it completely into the iodide. Excess of the methyl iodide was then evaporated off, and the veratrine compound treated with ether to remove any trace of the unchanged alkaloid. The iodide thus obtained was a light-yellow, crystalline powder, insoluble in ether and chloroform, and soluble in methyl and ethyl alcohols. It is soluble in hot water, from which it can be obtained as an almost white, crystalline powder. It melts at 210°–212° with apparent decomposition.

It contains $1\frac{1}{2}$ molecules of water of crystallization which can be removed by drying at 100°.

I. 0.3547 gram dried to constant weight at 100° lost 0.0132 gram H_2O.

II. 1.1180 grams dried to constant weight at 100° lost 0.0431 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9.CH_3I + 1\frac{1}{2}H_2O$.	I.	Found. II.
$1\frac{1}{2}H_2O$	3.55	3.72	3.85

Analyses gave the following numbers :

I. 0.2131 gram dried substance gave 0.4243 gram CO_2, and 0.1440 gram H_2O.

II. 0.2034 gram dried substance gave 0.0638 gram AgI.

	Calculated for $C_{32}H_{49}NO_9CH_3I$.	I.	Found. II.
C	54.03	54.28	....
H	7.1	7.35	....
I	17.32	....	16.94

Veratrine Methyl Hydroxide, $C_{32}H_{49}NO_9.CH_3OH$.—It was found that the iodine in the veratrine methyl iodide could be removed by treating with sodium or potassium hydroxide. The iodide was dissolved in water and dilute sodium hydroxide cautiously added. The solution soon began to turn brown and after several hours complete decomposition had taken place. Examination showed that two distinct substances had been formed—a waxy substance which refused to crystallize, and a crystalline substance which was sparingly soluble in water. The reaction seemed deep-seated, but it is probably closely associated with that given by Wright in the preparation of cevine by saponification.

A solution of the methyl iodide compound was again treated with freshly precipitated silver oxide and warmed. It was found that above 45° the solution again turned brown, indicating decomposition. The experiment was repeated without warming the solution. Five grams of the methyl iodide compound were placed in a shaking-flask with 200 cc. water, an excess of silver oxide added, and shaken for twelve hours at the ordinary temperature. At the end of that time the reaction seemed to be complete. The silver iodide and excess of silver oxide were removed by filtration. An attempt to concentrate a part of the clear solution by evaporating on a water-bath proved unsuccessful, for between 40° and 65° decomposition began, and in a half hour the whole solution became almost black.

A second portion of the clear solution was evaporated at the ordinary temperature. At the end of three days a residue was obtained as a white granular powder. The substance proved to be exceedingly unstable, turning gray and finally brown on gently warming. It is soluble in water, methyl and ethyl alcohols, and in acetone; slightly soluble in ether and chloroform. It differs materially from veratrine. It is not sternutatory, and appears to be physiologically inactive. It changes to a brown mass between 80° and 90°, but does not finally melt until the temperature is raised to 188°–190°. It contains water of crystallization, which was removed by heating in an air-bath at 60° for two hours. More satisfactory results, however, were obtained by drying over sulphuric acid *in vacuo*.

0.3958 gram dried to constant weight, lost 0.0320 gram H_2O.

	Calculated for $C_{32}H_{48}NO_9.CH_3 + 3H_2O$.	Found.
$3H_2O$	8.2	8.09

0.2022 gram dried substance gave 0.4828 gram CO_2, and 0.1557 gram H_2O.

	Calculated for $C_{32}H_{48}NO_9.CH_3$.	Found.
C	65.45	65.13
H	8.43	8.01

The apparent change which took place in the substance on drying is evidently deep-seated. The white granular substance on drying became a fine, light-gray, amorphous powder which is only slightly soluble in water. These changes, together with the comparative ease with which the substance decomposes, indicate that a part of the water exists as water of constitution. This supposition is confirmed by the analyses.

Veratrine Methyl Hydroxy Hydrochloride, $C_{32}H_{49}NO_9.CH_3$ OH.HCl.—Veratrine methyl hydroxide is very soluble in dilute acids and readily decomposed by strong acids. Sulphuric acid decomposes it, changing it first to a bright-red color, and finally, with decomposition, to a black, tar-like mass. Hydrochloric acid gives a red color if the acid is strong. Very

dilute acid dissolves it, leaving a perfectly clear solution. If this clear solution is allowed to evaporate spontaneously, a light-gray granular powder is formed. It is soluble in water, and can be obtained by spontaneous evaporation. It is soluble in methyl and ethyl alcohols. It forms a light, amber-colored varnish on evaporating off the alcohol. It is very unstable, decomposing below $100°$. It seemed to change upon standing over sulphuric acid for some time.

0.2065 gram substance, dried over sulphuric acid, gave 0.4444 gram CO_2, and 0.1311 gram H_2O.

	Calculated for $C_{32}H_{49}NO_9.CH_3OH.HCl.$	Found.
C	60.00	58.67
H	8.24	6.6

It is evident that the water of constitution is held more firmly here than in the free base.

Gold Double Salt, $(C_{32}H_{49}NO_9.CH_3OH.HCl)AuCl_3$.—An attempt to make the gold double salt from the hydrochloride did not prove successful. A decomposition took place on adding the gold chloride, apparently caused by excess of acid. A better method was found by treating the methyl hydroxide compound with gold chloride which had been rendered slightly acid with hydrochloric acid. A beautiful, lemon-yellow, crystalline powder was formed. It was filtered off, washed with hot water, and dried on an unglazed porcelain plate. The substance thus purified melted at $149°$. It is soluble in alcohol, but sparingly soluble in water, ether, and chloroform. It is comparatively stable, remaining unchanged at $110°$. A determination of water of crystallization was not made. A gold determination gave the following:

0.1716 gram dried salt gave 0.0362 gram Au.

	Calculated for $(C_{32}H_{49}NO_9.CH_3OH.HCl)AuCl_3$.	Found.
Au	20.37	21.09

Veratrine Ethyl Bromide, $C_{32}H_{49}NO_9.C_2H_5Br$.—Veratrine dissolves readily in ethyl bromide, and combines slowly to form the bromide. It was found that heating on a water-bath with reflux condenser for six hours was necessary to convert it all into the ethyl compound. At the end of the

reaction, the excess of ethyl bromide was evaporated off, leaving the veratrine ethyl bromide as a light-yellow, amorphous mass. By treating with water and stirring for some time, the substance was obtained in crystalline form. It is sparingly soluble in water, but readily soluble in methyl and ethyl alcohols. It decomposes readily. It shows signs of decomposition at 60°, and at 100° it seems completely changed. It does not finally melt, however, until a temperature of 160° is reached. The substance purified by boiling water was dried and analyzed. The result showed that decomposition had taken place, and that a tetrabromide of veratrine was formed. The odor of ethylene was noticed during the boiling. Analysis of the substance thus treated with water gave the following numbers :

I. 0.2270 gram dried substance gave 0.4591 gram CO_2, and 0.1603 gram H_2O.

II. 0.2228 gram dried substance gave 0.0200 gram AgBr.

	Calculated for $C_{32}H_{49}NO_9C_2H_5Br$.	I.	Found. II.
C	42.15	42.55	....
H	5.38	7.84	....
Br	35.06	....	38.73

Veratrine Allyliodide, $C_{32}H_{49}NO_9.C_3H_5I.$ — By digesting veratrine with allyl iodide on a water-bath for several hours, a solid, but slightly waxy-looking, substance was formed. The excess of iodide was removed and the substance washed thoroughly with ether. The iodide thus formed appeared partially crystallized, but changed, on standing in the air, to a semiwaxy mass. Exposed for some time to the air, or when stirred with water, the substance again becomes granular. The substance was finally obtained pure by dissolving in a small quantity of alcohol and precipitating with excess of ether. It thus appears as an almost white, crystalline powder. It is soluble in methyl and ethyl alcohols, and acetone. It melts at 235°–236° C., and contains 1 molecule of water which can be driven off at 100° C.

I. 0.1990 gram dried substance gave 0.4000 gram CO_2, and 0.1202 gram H_2O.

II. 0.3022 gram dried substance gave 0.0954 gram AgI.

	Calculated for $C_{32}H_{49}NO_9.C_3H_5I$.	I.	II.
C	55.29	54.81	....
H	7.1	6.71	....
I	16.73	....	17.04

An attempt to obtain the free base by shaking with silver oxide was unsuccessful. The solution turned brown at the ordinary temperature and had the odor of allyl alcohol.

Several experiments have been made by heating the alkaloid at different temperatures. In each case a beautifully crystallized substance was obtained which gave all the characteristics of veratric acid. Experiments are now being carried on along this line.

LIX.—ON THE ACTION OF HYDROGEN SULPHIDE UPON VANADATES.

By James Locke.

The fact that pentavalent vanadium, in contradistinction from niobium and tantalum, the other members of the group to which this element belongs in the Periodic System, readily forms salts derived from sulphovanadic acids, was first shown conclusively by Krüss and Ohnmais[1] in 1891. These authors investigated very thoroughly such sulphovanadates as they were able to prepare by the wet methods and isolated a number of well-crystallized compounds, such as $(NH_4)_3VS_4$, $Na_3VS_3O + 5H_2O$, $Na_3VO_3S + 10H_2O$, etc. These experiments were supplemented, in 1893, by some work carried out by Krüss[2] alone, on the formation of the same class of salts in reactions in the dry way.

By fusing vanadium pentoxide with sodium carbonate and a large excess of sulphur, until the latter was nearly driven off, and then washing the residue alternately with carbon disulphide and alcohol, he obtained as a residue a brownish-red, crystalline powder. This dissolved readily in water, forming a deep-red or purple solution, and showed the various other properties of the salt, Na_3VOS_3, which in the hydrated form he had previously obtained in the wet way.

[1] Ann. Chem. (Liebig), **263**, 40–72.　　[2] Ztschr. anorg. Chem., **3**, 264.

Halberstadt[1] has shown that vanadium trichloride can readily be obtained by the direct action of chlorine upon the trisulphide. This reaction suggested to me the possibility of preparing the same substance directly from a sodium or potassium vanadate, by first converting the latter into a sulpho-salt free from oxygen, and then treating the latter with chlorine.

With this end in view, I first submitted sodium orthovanadate, Na_3VO_4, to the action of hydrogen sulphide. The reaction did not proceed exactly as I had hoped, but as the behavior of vanadates upon ignition in an atmosphere of hydrogen sulphide has not hitherto been investigated, a communication of my results may be of some interest. A weighed quantity of the orthovanadate, very carefully dried, was introduced, in a porcelain boat, into a combustion tube, and first submitted to the action of the gas in the cold. A reaction at once set in, but owing to the protective coating of sulphovanadate formed upon the salt, it soon ceased. In order to obtain a homogeneous product, it was found necessary to heat the boat at a temperature of from 500°–700°. At this temperature the absorption of the hydrogen sulphide was almost violent, and care was required to prevent loss due to the spattering of the molten salt. The reaction subsided in a short time, although repeated weighings showed that a slight absorption was still taking place, and the contents of the boat continued slowly to gain in weight for some hours.

The final result was as follows:

	Grams.
Weight of sulphovanadate formed	1.4256
" " Na_3VO_4 taken	1.1390
Increase in weight	0.2866
	= 26.04 per cent.

The increase calculated for the reaction,

$$Na_3VO_4 + 3H_2S = Na_3VOS_3 + 3H_2O,$$
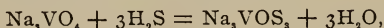
is 26.07 per cent. The product possessed all the characteristic properties which Krüss had previously observed in the salt Na_3VOS_3, and was undoubtedly identical with that compound.

[1] Ber. d. chem. Ges., **15**, 1619 (1882).

The fact that both by his method and the above, a complete substitution of sulphur for oxygen could not be obtained in the ortho salt, led me to make a similar experiment with sodium pyrovanadate, $Na_4V_2O_7$. An analogous reaction would here lead to the formation of a salt containing two residual atoms of oxygen. This was found to be the case. The hydrogen sulphide was allowed to pass over the molten salt for six hours; the latter was then weighed, and subsequently treated with the gas for two hours more. No gain was observed to have taken place after the first weighing:

	Grams.
Weight of product	1.1974
" " $Na_4V_2O_7$ taken	0.9536
Increase	0.2438
	$= 25.67$ per cent.
Calculated increase, $Na_4V_2O_7$	
to $Na_4V_2O_2S_5$	$= 25.93$ " "

This compound, which was not described by Krüss, resembles very closely the other sulphovanadates of the alkali metals. It is easily fusible to a dark, brownish-red liquid, which on cooling solidifies to a highly crystalline mass, the latter being very similar to potassium permanganate in color and luster. When the heated salt is exposed to the air it at once takes fire, giving off sulphur dioxide and yielding as a residue sodium hypovanadate. The salt is exceedingly hygroscopic, and when first dissolved in water forms a deep reddish-purple solution. This changes rapidly in color, however, hydrogen sulphide being given off, and the solution, after passing through various shades of red and pink, becomes colorless. The formation of a colorless sodium vanadate solution in this way would indicate that the first decomposition reaction is simply one of gradual substitution of oxygen for sulphur in the sulphovanadate, according to the equation,

$$Na_4V_2O_2S_5 + H_2O = Na_4V_2O_3S_4 + H_2S, \text{ etc.}$$
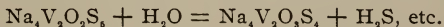
Reduction of the vanadic acid to the vanadyl state takes place only subsequently; the solution then turns to green, and finally blue, with deposition of free sulphur.

The gradual passage of the sulphovanadate into the vana-

date is accompanied by a remarkable alteration in the color of the free sulphovanadic acid which separates out on addition of hydrochloric acid. When obtained from a freshly prepared solution, this precipitate is black; from one which has been standing a short time it comes down dark-yellow; and from the nearly oxidized solution it is of a pale orange color. This transition in color from the acids containing much sulphur to those containing little is well seen in the products obtained when a combustion tube is filled with sodium vanadate and submitted to the action of hydrogen sulphide for an hour or two. At first the entire contents of the tube became uniformly brown. But, as heat is applied and the water formed in the anterior portion of the tube reacts with the sulpho-salt in the posterior end, the latter gradually loses color again. The acids obtained by treating the solution of successive portions of the product then show the same gradations in color as do those obtained as before described. Unfortunately, all these acids are so unstable as to render their isolation in the pure state practically impossible. Several attempts were made to obtain them, but without success. Sulphur determinations in a number of precipitates, after careful washing with carbon disulphide, gave values lying between those calculated for the compounds $H_4V_2O_5S_6$ and $H_4V_2O_4S$, but they pointed to the presence of no single acid.

Finally, it must be remarked that in company with Mr. J. S. North, I have tried to prepare the sulphovanadates of several of the heavy metals by the above method. The substitution seems in this case to be less complete than when sodium or potassium vanadate is used, this being probably due to the fact that the vanadates of the heavy metals are not fusible. Lead vanadate alone yielded what seemed to be a definite compound. On subjecting lead pyrovanadate to the action of hydrogen sulphide at a full red heat, the salt at first fused and then solidified again to a crystalline, black powder of high luster. It was then found to have gained 5.31 per cent. in weight. The increase calculated for the conversion of $Pb_2V_2O_7$ into $Pb_2V_2O_6S_2$ is 5.01 per cent., and it is probable, therefore, that the latter is the formula of the product.

ON THE FORMATION OF IMIDO-1,2–DIAZOL DE-RIVATIVES FROM AROMATIC AZIMIDES AND ESTERS OF ACETYLENECARBOXYLIC ACIDS.

By A. Michael, F. Luehn, and H. H. Higbee.

Several years previous to the discovery of hydrazine one of us[1] endeavored to obtain this base by introducing a nitro group into phenylhydrazine, and treating the nitro product with alkalies or acids. At the same time, a series of experiments were made to reduce phenylazimide, but it was found impossible to effect a reduction of this substance without its breaking down to aniline ; a decomposition which had been previously described. The reduction of phenylazimide was again attempted, some years later, in a different manner ; starting with the idea that if the nitrogen-chain could be broken by addition of some reagent, it might be possible to reduce, and then decompose, the addition-product. Phenylazimide showed itself to be indifferent, at a moderate temperature, to reagents that, in other compounds, are added to unsaturated nitrogen, and at a higher temperature it decomposed. On the other hand, the tendency of nitrogen and carbon to form five-membered rings, showed itself in the remarkable ease with which phenylazimide can be added to esters of $\Delta\alpha\beta$-acids of the acetylene series, and this reaction forms the subject of the present paper. These addition-products no longer show the instability that characterizes the tri-nitrogen-ring, but they are stable towards heat and towards most reagents. It is possible to reduce them, but the hydrogen is added to the unsaturated carbons, and the attempt to effect a further reduction, by the use of strong reducing agents at a higher temperature, was followed by the breaking down of the ring to aniline. The reaction between phenylazimide and acetylene-dicarboxylic ester presents a striking analogy to that of diazo-acetic and acetylenedicarboxylic esters.[2] The latter reaction takes place by disruption of linkage between carbon and nitrogen to form a five-membered ring, the other possible re-

[1] A. Michael : Ber. d. chem. Ges., 19, 1386.
[2] Buchner : Ann. Chem. (Liebig), 273, 214.

action being less favored, as it would lead to the formation of a four-membered ring :

$$\underset{\underset{N-N}{\overset{\overset{\displaystyle COOC_2H_5}{|}}{C}}}{\bigwedge} \quad + \quad \underset{C-COOC_2H_5}{\overset{C-COOC_2H_5}{\cdot | \cdot}} \quad = \quad N \underset{N-C-COOC_2H_5}{\overset{CH-C-COOC_2H_5}{\underset{\cdot | \cdot}{<}}}$$
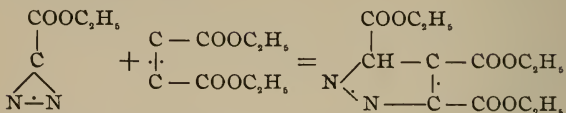
Owing to the accumulation of negative groups around the methine of this primary product, its hydrogen is very reactive, and, as the product also contains an easily reducible azogroup, a spontaneous atomic rearrangement occurs, in which the methine-hydrogen passes over to the most negative of the nitrogen atoms, with consequent shifting of unsaturation :

$$N \underset{N-C-COOC_2H_5}{\overset{CH-C-COOC_2H_5}{\underset{\cdot | \cdot}{<}}} \quad \rightarrow \quad N \underset{NH-C-COOC_2H_5}{\overset{C-C-COOC_2H_5}{\underset{\cdot | \cdot}{<}}}$$
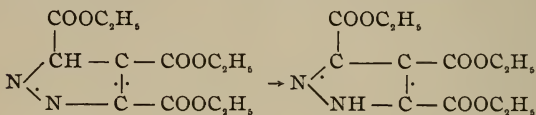
It is evident from the constitution of our addition-product that an intramolecular conversion of the azo into a hydrazine derivative is not possible, as the product does not contain hydrogen in the ring :

$$H_5C_6-N \underset{N}{\overset{N}{<}} \underset{\cdot | \cdot}{+} \underset{C-COOC_2H_5}{\overset{C-COOC_2H_5}{\cdot | \cdot}} = H_5C_6-N \underset{\underset{H_5C_2OOC}{\overset{C}{\overset{|}{\div}} \underset{COOC_2H_5}{C}}{\overset{N \div N}{<}}$$
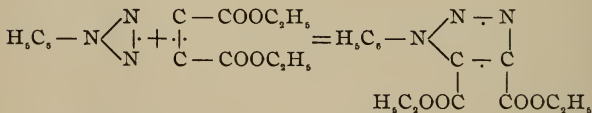
In the above reaction there is a possibility of a four-membered ring being formed, and, although from theoretical reasons, such a ring formation seems improbable, it is desirable to connect the substances we have obtained with imidodiazol derivatives obtained by a different method. Several months previous to the preliminary notice[1] on this reaction, Bladin[2] published a short note on the oxidation of azimidotoluene, in which he described a triazoldicarboxylic acid obtained in this manner. The constitution of this acid depends on that of azimidotoluene, and there are two formulas that have been assigned to it :

[1] A. Michael: J. prakt. Chem. [2] **48**, 94. [2] Ber. d. chem. Ges., **26**, 545.

I.   II.

$$H_3C-C_6H_3\left\langle \begin{array}{c} N \\ NH \end{array} \right\rangle N \qquad H_3C-C_6H_3\left\langle \begin{array}{c} N \\ | \\ N \end{array} \right\rangle NH$$
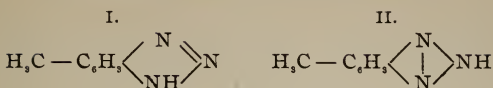
The first of these was given by Kekulé,[1] but it was subsequently rejected by Griess,[2] as he found that the same carbamylazimidobenzoic acid[3] is formed from the isomeric 1,3,4- and 1,4,3-amidouramidobenzoic acids, whereas, according to Kekulé's interpretation of the reaction, different carbamylazimido acids should be formed:

$$C_6H_3 \begin{array}{l} \diagup COOH \quad (1) \\ -NCONH_2, \quad (3) \\ \diagdown N \diagup\!\!\!\diagup N \quad (4) \end{array} \qquad C_6H_3 \begin{array}{l} \diagup COOH \quad (1) \\ -N \diagdown N \quad (3) \\ \diagdown NCONH_2 \quad (4) \end{array}$$
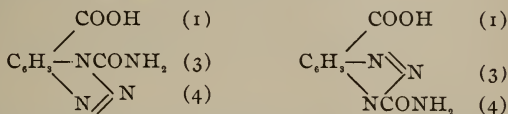
Unfortunately Griess published only a preliminary note on this work, so that a strict proof of the identity of the products obtained from the isomeric acids is wanting. It is also difficult to understand the formation of a compound having the constitution which Griess assigned to carbamylazimidobenzoic acid,

$$C_6H_3 \begin{array}{l} \diagup COOH \\ -N \diagdown \\ \diagdown N \diagup \end{array} N-CONH_2,$$
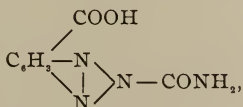
as it implies a separation of carbamyl from the nitrogen to which it is joined in the amidouramidobenzoic acids. If the carbamylazoimidobenzoic acids are, as seems not unlikely, isomeric, but very similar products, it would not be difficult to understand that the azimidobenzoic acids

I.   II.

$$C_6H_3 \begin{array}{l} \diagup COOH \quad (1) \\ -NH \quad (3) \\ \diagdown N \diagup\!\!\!\diagup N \quad (4) \end{array} \qquad C_6H_3 \begin{array}{l} \diagup COOH \quad (1) \\ -N \diagdown N \quad (3) \\ \diagdown NH \quad (4) \end{array}$$
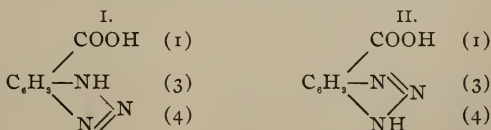
[1] Lehrb. org. Chemie, II, 739.   [2] Ber. d. chem. Ges., **15**, 1879.
[3] Griess called this compound azimidouramidobenzoic acid, which is evidently a misnomer, as it does not contain an uramido group. If the radical of carbamic acid is called, according to the usual manner of designating an acid radical, carbamyl, the above name correctly represents the constitution of the substance.

should pass over into one stable modification, it being by no
means impossible that a substance with the constitution I.
would pass over into that of II. by intramolecular reduction,
and consequent shifting of linkage or *vice versa*. Accordingly,
whether Kekulé's or Griess' conceptions of the constitution of
azimidotoluene is accepted, the constitution of Bladin's acid
may be represented as follows :

HN
$\begin{array}{l} \diagup \text{N—C—COOH} \\ \qquad | \cdot \\ \diagdown \text{N—C—COOH} \end{array}$
      HN
$\begin{array}{l} \diagup \text{N—C—COOH} \\ \quad | \quad | \cdot \\ \diagdown \text{N—C—COOH} \end{array}$

To ascertain whether the compound from phenylazimide
and acetylenedicarboxylic ester is a derivative of the same
ring as Bladin's acid, we oxidized the aromatic nucleus to
two carboxyls, after having introduced a nitro group into it
and conversion of this into an amido group, and we found the
dibasic acid thus formed to be identical with Bladin's tri-
azoldicarboxylic acid.

In the reaction of phenylazimide towards acetylenedicar-
boxylic ester we have the analogy with diazoacetic ester,
where the link between carbon and nitrogen is severed, as this
addition-product undoubtedly does not contain a tri-membered
ring, which would be the case if the addition went by union
of unsaturated nitrogens to unsaturated carbons. However,
when one considers the tendency of nitrogen to form a tri-
ring, it is by no means impossible that a five-membered triazol
ring, containing two nitrogens joined together to form a
tri-ring, may exist.[1] In this paper we shall consider our
products as derived from an open five-membered ring, but we
cannot consider this view of their constitution as having been
definitely established, and we believe it is more a question of
probability than of exact proof.

Action of Phenylazimide[2] on Methyl Acetylenedicarboxylate.

If these substances are allowed to stand for some days at
ordinary temperature, large crystals are slowly deposited, but
under these conditions the addition takes place very slowly.
The reaction occurs somewhat more quickly if the mixture is
placed in strong sunlight, but this acceleration may be due

[1] A somewhat analogous constitution is supposed to exist in the ketines.
[2] Phenylazimide should be made from phenylhydrazine, freshly distilled in a

to a rise in temperature, and not to the actinic influence of sun-
light. The addition proceeds quite rapidly at 100°, and to
prepare the substance equivalent amounts of phenylazimide
and acetylenedicarboxylic methyl ester, diluted with an equal
weight of carbon tetrachloride, are heated to 100° in a flask
connected with an inverted cooler for five hours. On cooling
a copious precipitate is deposited, which, filtered and washed
with ether, gives the addition-product in pure condition. A
small amount of the substance may be obtained from the
mother-liquor by concentration. The yield is about 80 per
cent. of the theoretical. For analysis it was recrystallized
from alcohol and dried at 100°.

I. 0.2251 gram substance gave 0.4572 gram CO_2, and 0.0914
gram H_2O.

II. 0.3272 gram substance gave 44.5 cc. N at 13° C. and
765.5° mm.

	Theory for $C_6H_5-N_3C_2(COOCH_3)_2$.	Found.
C	55.17	55.39
H	4.21	4.52
N	16.09	16.18

The product forms white needles, that melt without de-
composition at 127°–128°. It is insoluble in water, sparingly
in carbon tetrachloride and ether in the cold, and has neu-
tral properties.

To obtain the acid corresponding to this ester, a mixture
of 24 grams ester, 19.2 grams potassium hydroxide, and 60
grams 70 per cent. alcohol, were heated four hours on a water-
bath, the solution concentrated, and the acid precipitated by
a mineral acid. After several crystallizations from water the
product was in pure condition.

I. 0.1852 gram substance, dried at 100°, gave 0.3499 gram
CO_2, and 0.0547 gram H_2O.

vacuum, as otherwise it may contain aniline, which it is difficult to separate by dis-
tillation. We found the following directions gave the best yield of acetylenedicar-
boxylic ester. 25 grams acid, 70 grams methyl alcohol, and 4 grams sulphuric
acid were heated for 45 minutes in a water-bath with an inverted cooler. The prod-
uct was heated with slanting cooler as long as alcohol passed over readily, then
thrown into water and the mixture extracted with ether. The ethereal solution
was extracted with sodium carbonate, which removed considerable acid-ester and
which may be used for the preparation of neutral ester. The neutral ester is frac-
tionated in a vacuum several times to remove higher boiling products.

II. 0.2757 gram substance, dried at 100°, gave 43.8 cc. N at 15° C. and 748 mm.

	Theory for $C_8H_5N_3C_2(COOH)_2$.	Found.
C	51.50	51.53
H	3.00	3.27
N	18.03	18.31

The acid crystallizes from water in long, prismatic needles that resemble those of phthalic anhydride, and melts with decomposition at 149°–150°. It is moderately soluble in cold water, more easily in alcohol, and readily in hot water.

A neutral solution of the potassium salt shows the following behavior towards metallic salts :

$BaCl_2$: On mixing the solutions a white crystalline precipitate of the barium salt is deposited, which consists of short plates, sparingly soluble in cold water.

$MgCl_4$: No precipitate.

$CuSO_4$: No precipitate.

$CdSO_4$: Slight precipitate of colorless groups of crystals.

$Pb(NO_3)_2$: White, crystalline precipitate.

Fe_2Cl_6 : Yellowish precipitate with crystalline structure.

The silver and calcium salts were analyzed.

Silver Salt.—Fine, white needles, that are sparingly soluble in cold water.

I. 0.6721 gram, air-dried, silver salt lost 0.0290 gram H_2O at 100°, and could not be heated higher without decomposition.

II. 0.6431 gram salt, dried at 100°, gave 0.3106 gram silver.

	Theory for		Found.
	$C_{10}N_3O_4H_5Ag_2.H_2O$.	$C_{10}N_3O_4H_5Ag_2$.	
H_2O	3.87	....	4.31
Ag	....	48.59	48.29

Calcium Salt.—White, truncated prisms, that are grouped in star-like forms, and are moderately soluble in cold water.

I. 0.4000 gram air-dried salt lost 0.099 gram water at 135°.

II. 0.3010 gram salt, dried at 135°, gave 0.1515 gram $CaSO_4$.

	Theory for		Found.
	$C_{10}N_3O_4H_5Ca.5H_2O$.	$C_{10}N_3O_4H_5Ca$.	
H_2O	24.93	....	24.75
Ca	....	14.75	14.77

The acid melts with partial decomposition, and with evolution of carbon dioxide. To study this reaction a portion of the acid was heated to 150° in a metal bath as long as carbon dioxide came off, and the residue, which solidified on cooling, together with the portion that had sublimed into the upper part of the flask, was extracted with aqueous sodium carbonate, and the residue then crystallized three times from hot water. An analysis of this product gave the following figures :

0.1635 gram vacuum-dried substance gave 0.3975 gram CO_2, and 0.0770 gram H_2O.

	Theory for $C_6H_8N_2C_2H_2$.	Found.
C	66.23	66.29
H	4.82	5.22

The substance forms white crystals, that are moderately soluble in cold, readily in hot, water or alcohol, and melt, without decomposition, at 55°–56°. It volatilizes with steam with a pleasant, aromatic odor. In the decomposition of the dibasic acid both of the carboxyls have been removed, and the product therefore has not acidic properties ; but, on the other hand, it shows the properties of an imidodiazol, inasmuch as it dissolves in hydrochloric acid, and is not precipitated by water from this solution. The basic properties, however, are so slightly developed that the hydrochlorate only exists in solution, and evaporation of this solution in a vacuum leaves the original substance. A double salt with platinic chloride is obtained by adding the chloride to the hydrochloric acid solution of the compound, and washing the precipitate with dilute hydrochloric acid. It forms long, prismatic needles, which, after drying first in a vacuum, then at 100°, were analyzed :

I. 0.5950 gram vacuum-dried salt lost 0.0115 gram H_2O at 100°.

II. 0.5835 gram salt, dried at 100°, gave 0.1640 gram Pt.

	Theory for $(C_8H_8N_2)_2PtCl_6.H_2O.$	$(C_8H_8N_2)_2PtCl_6.$	Found.
H_2O	2.52	....	1.93
Pt	....	27.84	28.01

The dibasic acid described above is isomeric with the

n-phenylosotriazoldicarboxylic acid of Pechmann.[1] An ester of this acid would be formed in the reaction of phenylazimide on acetylenedicarboxylic ester, by assuming that the addition occurs through disruption of the unsaturated nitrogen:

$$C_6H_5-N\begin{matrix}N\\ \\N\end{matrix}\begin{matrix}C-COOCH_3\\+\\C-COOCH_3\end{matrix} = C_6H_5-N\begin{matrix}N-C-COOCH_3\\ \\N-C-COOCH_3\end{matrix}.$$
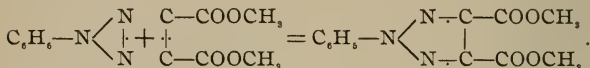
A comparison of the properties of Pechmann's with those of our acid shows conclusively that they are not identical, and there are therefore only the two constitutions already considered that are possible for our product. Since the single-chain triazol constitution is at present the more probable, we shall consider our substances as derivatives of this body. According to this conception the dibasic acid may be called *n*-phenyl-1,2-imidodiazoldicarboxylic acid,[2] and its decomposition by heat may be represented as follows:

$$H_5C_6-N\begin{matrix}N-N\\ \\C-C-COOH\\ \\HOOC\end{matrix} = H_5C_6-N\begin{matrix}N-N\\ \\CH-CH\end{matrix} + 2CO_2.$$
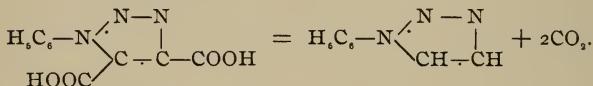
The basic compound is therefore *n*-phenyl-1,2-imidodiazol, and it shows the stability towards bases and acids which characterizes the imidodiazol ring. Even towards oxidizing agents it shows itself as a very stable substance. A portion of the compound was heated for ten hours with an excess of potassium permanganate, and, after the excess of permanganate was removed by addition of sufficient alcohol, the liquid was found to contain considerable unchanged substance, besides oxalic acid and a small amount of a second acid, which was not further examined.

Conversion of *n-Phenylimido-1,2-diazoldicarboxylic acid into Imido-1,2-diazoldicarboxylic Acid.*

We first attempted to remove the phenyl in the dibasic acid by oxidation. A solution of 2 grams of acid, 2 grams potas-

[1] Ann. Chem. (Liebig), **262**, 311.

[2] Of the various nomenclatures suggested for this and analogous classes of substances, that of deriving them from the radicals, 1-azole, —CH—CH—CH—N—, or from 2-azole, —CH . CH—N . CH—, seems the simplest.

sium hydroxide, 10.8 grams potassium permanganate (equivalent to 12 atoms oxygen to 1 molecule of acid) and 60 grams water was boiled six hours, when about 0.1 of the permanganate was still unacted on. The excess of oxidizing agent was removed by alcohol, and the liquid, after filtration, concentrated, acidified with acetic acid, and calcium acetate added. After filtration from the calcium oxalate, the filtrate was acidified with nitric acid, and a concentrated solution of silver nitrate added, when a precipitate of a silver salt was deposited. This salt was treated in the cold with concentrated chlorhydric acid, an equal volume of water then added, and the mixture heated and filtered from silver chloride. On cooling a crystalline substance separated, which, after several crystallizations from dilute chlorhydric acid, melted at 146°–147°, and had the properties of the original dibasic acid. Its identity with the acid was further confirmed by decomposing a small quantity of the substance at 150°, when the basic phenylimidodiazol, melting at 55°–56°, was obtained. According to this result the dibasic acid is oxidized in alkaline solution with difficulty, with formation of oxalic acid.

Baltzer and Pechmann[1] succeeded in obtaining imido-1,4-diazolcarboxylic acid (osotriazolcarboxylic acid) by oxidation of amido-*n*-phenylimido-1,4-diazolcarboxylic acid ; the introduction of the amido group rendering the benzene-nucleus easily susceptible to oxidation, and we adopted this method to replace phenyl by hydrogen in our dibasic acid.

We first attempted to introduce a nitro group into the phenyl of the compound by direct treatment with a mixture of fuming nitric and concentrated sulphuric acids, varying the conditions of temperature and time, and, although a reaction took place, the yield of nitro product obtained was inconsiderable. The product formed in this way was crystalline, sparingly soluble in water, and melted at 204°.

We then attempted to prepare the ester of the nitro acid by addition of nitrophenylazimide to acetylenedicarboxylic ester, and with better success. When we began these experiments there were two methods known to prepare nitrophenylazimide, and preliminary experiments induced us to

[1] Ann. Chem. (Liebig), **262**, 314.

prepare the product by direct nitration.[1] Although we varied the conditions of the nitration we were not able to obtain more than 44 per cent. of the weight of phenylazimide in a pure nitro product; but as this is a somewhat better yield than had been previously obtained, we give the conditions observed in the nitration. To a well-cooled quantity of phenylazimide a cold mixture of twice the weight of fuming nitric acid and an equal weight of concentrated sulphuric acid was added in small portions at a time, the flask being well shaken after each addition, and care being taken to prevent the temperature of the contents of the flask from rising above $0°$ during the operation. The product was allowed to stand in ice for an hour, then poured into water, and steamed as long as the nitro product passed over. The crude product melted from $57°-66°$, but by several crystallizations from alcohol it became constant at $72°-73°$. Subsequently Noelting and Michel[2] published an excellent and much more convenient method of preparing this substance from p-nitrodiazobenzene sulphate and hydrazine, and we used their method to obtain the substance.

A solution of nitrophenylazimide and acetylenedicarboxylic methyl ester, in molecular proportions, in double the weight of dry benzene, was heated, in an open flask connected with an inverted cooler, for eight hours, and, after cooling, the light-brown precipitate was filtered under pressure and washed with a little dry benzene. The product thus obtained was pure, as shown by analysis:

I. 0.2020 gram substance, dried at $100°$, gave 0.3479 gram CO_2, and 0.0605 gram H_2O.

II. 0.1835 gram substance, dried at $100°$, gave 28.7 cc. N at $13°$ C. and 750 mm. pressure.

	Theory for $C_6H_4{<}^{NO_2}_{N_3C_2(COOCH_3)_2}$.	Found.
C	47.05	46.97
H	3.26	3.31
N	18.30	18.21

[1] Culmann and Gasiorowski: J. prakt. Chem., **40**, 116.
[2] Ber. d. chem. Ges., **26**, 90.

p-Nitro-*n*-phenylimido-1,2-diazoldicarboxylic methyl ester crystallizes from alcohol in needles, that melt at 117°–118°. It is moderately soluble in cold, easily in hot, benzene and hot alcohol; insoluble in water.

In saponifying this ester the use of alcoholic potash must be avoided, as complex decomposition-products are formed, probably in consequence of a partial reduction of the nitro group. Even when aqueous potash is used, certain precautions are necessary. The best results were obtained by heating 3 grams of ester, 2.7 grams caustic potash, and 90 grams water for an hour and a half, and testing at the end of that time whether any unchanged ester separated from a small portion of the liquid on cooling. If not, the solution was allowed to cool, and about one-half its volume of moderately strong chlorhydric acid added to it. On rubbing the sides of the vessel crystals separated, which were filtered and washed with a little water. These crystals left a trace of mineral matter when ignited; they were dissolved in a small amount of warm water, and an equal volume of hydrochloric acid added. The product deposited on cooling was crystallized from water and analyzed.

I. 0.1830 gram of substance, dried at 100° in a vacuum, gave 32.4 cc. N at 19°.5 C. and 764.5 mm.

II. 0.2336 gram of substance, dried at 100° in a vacuum, gave 43 cc. N at 19° C. and 754.5 mm.[1]

	Theory for $C_6H_4\big\langle{}^{NO_2}_{N_3C_2(COOH)_2}$		Found.
		I.	II.
N	20.14	20.42	20.95

The acid crystallizes from water in almost white plates and needles, the latter gradually passing over into the former on standing. It is moderately soluble in cold, easily in hot, water, very slightly in chlorhydric acid, and melts with decomposition at 162°–163°. To reduce the nitro acid it was gradually introduced (3.5 grams) into a warm solution of 9 grams hydrated stannous chloride in 15 grams concentrated chlorhydric acid, a fresh portion of the substance being

[1] In this determination a product was used that had lost a little carbon dioxide in treatment with too strong chlorhydric acid.

added only after reduction had taken place. On cooling and stirring the liquid a grayish salt separated, which was filtered and washed with concentrated chlorhydric acid. The salt was allowed to stand for an hour with an excess of ammonia, then filtered, the precipitate washed with water, and to the filtrate, after heating on a water-bath to drive off part of the free ammonia present, acetic acid was added. The straw-colored precipitate was filtered and washed. As it left a slight mineral residue on ignition, an attempt was made to remove the impurity by crystallizing from water. About one-half of the substance went into solution, but the dissolved part did not crystallize out when the solution became cold. On concentrating, straw-colored filaments and few prismatic crystals separated, which contained mineral matter, and when the concentrated solution was treated with glacial acetic acid in excess, a difficultly soluble precipitate was deposited, which is identical with the part of the original substance that did not dissolve in water, and which consisted of prismatic crystals. These crystals, being free of mineral matter, were recrystallized from considerable hot water, and analyzed.

0.1683 gram substance, dried at 100°, gave 34.2 cc. N at 21° C. and 759 mm.

	Theory for $C_6H_4\!\!<\!\!{}^{NH_2}_{N_3C_2(COOH)_2}$.	Found.
N	22.58	23.04

Amido-*n*-phenyl-1,2-diazoldicarboxylic acid separates from hot water in thick, prismatic crystals, that are quite insoluble in cold and only moderately in boiling water. The melting-point varies somewhat according to the rapidity of heating, being usually at 218°–219°, but it may melt as low as 214°–215° or as high as 225°–226°, according to the conditions. The substance shows acid and basic properties, dissolving in alkalies and mineral acids, but not, as is evident from its preparation, in acetic acid. We first endeavored to obtain imidodiazoldicarboxylic acid from the imido acid by following the directions given by Baltzer and Pechmann.[1] One gram of acid was dissolved in a solution of 1.4 grams caustic potash in 60 grams

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[1] Ann. Chem. (Liebig), **262,** 317.

water, and a saturated solution of potassium permanganate added, in small portions at a time, until no further oxidation took place in the cold, when it was continued for an hour in a hot water-bath. During the operation the solution was kept alkaline by addition of caustic potash. The solution was decolorized by alcohol, filtered from manganese dioxide. The filtrate was slightly acidified by acetic acid, filtered from a gelatinous orange-colored substance, and the oxalic acid formed in the oxidation precipitated by calcium chloride. The filtrate from the calcium oxalate was treated with cupric acetate, when a voluminous, blue precipitate was deposited, which, after washing, was suspended in water, decomposed by hydrogen sulphide, and the filtrate from copper sulphide concentrated when white crystals separated on cooling. This substance contained mineral matter, which could not be removed by crystallization from chlorhydric acid, and the yield of it obtained was so small that this method of oxidation and treatment was given up. A more satisfactory result was obtained by following the method used by Bladin[1] in the oxidation of azimidotoluene. Portions of 3 grams of amido acid were dissolved in 12 grams of a 10 per cent. solution of sodium hydrate, and a warm concentrated solution of permanganate added to the solution, until no further oxidation took place. The excess of oxidizing agent was removed by alcohol, and the manganese dioxide separated by filtration. As the dioxide retains some of the oxidation-product it was extracted with boiling water, and the filtrate from it added to the first filtrate. The pale green solution was made slightly acid with acetic acid, concentrated to a small bulk, and an excess of acetic acid added. The orange-colored precipitate was filtered, and a considerable excess of nitric acid, then a solution of silver nitrate added to the filtrate. A yellowish precipitate of silver salt was deposited, which was decomposed by warming with an excess of dilute chlorhydric acid, and the filtrate from silver chloride concentrated, when a white crystalline substance separated on cooling. The yield was small, only 1 gram of acid from 6 grams of amido compound. For analysis it was recrystallized.

[1] Ber. d. chem. Ges., **26**, 545, 2736.

0.1618 gram acid, dried at 100°, gave 0.1829 gram CO_2, and 0.0279 gram H_2O.

	Theory for $N_3HC_2(COOH)_2$.	Found.
C	30.57	30.82
H	1.91	1.91

The acid forms prismatic crystals, that melt, with decomposition and evolution of carbon dioxide, at 200°–201°. It is easily soluble in hot water and cold acetic ester, also in hot strong chlorhydric acid; only slightly soluble in hot chloroform and carbon tetrachloride.

A portion of the acid was neutralized by ammonia, and gave the following tests:

$AgNO_3$: Voluminous, pale-yellow precipitate, almost insoluble in nitric acid.

$BaCl_2$: Heavy white crystalline powder, without discernible crystalline form, but on standing it gradually goes over into tufts of acicular crystals.

$CaCl_2$: White groups of spear-like plates that are difficultly soluble in water.

$CuSO_4$: Light-blue precipitate of granular crystals that are easily soluble in mineral acids and ammonia.

The acid potassium salt was made by dissolving the acid in a slight excess of caustic potash and then adding dilute chlorhydric acid until the solution gave a slightly acid reaction for the mineral acid, when it separated as microscopic needles, that are moderately soluble in cold and easily in hot water. The salt contains one molecule of water of crystallization.

0.3126 gram air-dried salt lost 0.0261 gram water at 100°.

	Theory for $C_4N_3O_4H_2K.H_2O$.	Found.
H_2O	8.45	8.03

A comparison of the properties of this acid with the triazoldicarboxylic acid obtained by Bladin[1] by the oxidation of azimidotoluene leaves no doubt that the substances are identical, and, assuming the open five-membered ring constitution for our imidodiazol derivatives, the formation of the acid may be represented as follows:

[1] Ber. d. chem. Ges., **26**, 545 and 2736.

$$C_6H_4 \big\langle \begin{smallmatrix} NH_2 \\ N \end{smallmatrix} \begin{smallmatrix} N—N \\ | \end{smallmatrix} \quad + 2H_2O + 10O =$$
$$HOOC—C \doteq C—COOH$$

$$HN \big\langle \begin{smallmatrix} N——N \\ | \end{smallmatrix} \begin{smallmatrix} C \doteq C \\ | \quad | \end{smallmatrix} \quad + 3C_2O_4H_2 + NH_3.$$
$$COOH \; COOH$$
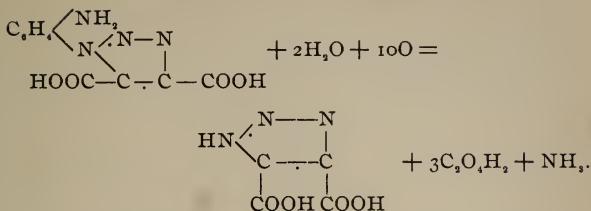
In the preparation of imidodiazoldicarboxylic acid, we mentioned a voluminous substance which was precipitated when acetic acid is added to the oxidized product. The substance, which is formed in considerable amount, as we obtained 1.4 grams of it in oxidizing 3 grams amido acid, forms an orange-red body, that does not melt when heated, but swells up and turns to a black mass, and heated higher it burns leaving a mineral ash. To free it from mineral matter it was digested for a half hour with moderately strong hydrochloric acid, the insoluble part washed with water, and crystallized from a considerable amount of hot water. It forms orange-red, granular crystals, that begin to darken at 326°, and melts at 328°–330°, with decomposition. The following analysis does not agree with any simple decomposition-product of the amido acid, and want of time prevented a further investigation of the substance.

0.1644 gram substance, dried at 100°, gave 0.2738 gram CO_2 and 0.0453 gram H_2O.

C	45.42
H	3.06

Nitrophenylimidodiazoldicarboxylic acid decomposes, with evolution of carbon dioxide, more easily than the mother-acid, and a few minutes' heating at 160° suffices to effect complete decomposition. The dark-brown residue was extracted with hot alcohol, and, as the new substance is only slightly soluble in the hot solvent, it was found advisable to filter the alcohol while hot, and, after cooling and removal of the precipitate by filtration, again extract with the same alcohol, repeating the operation until all the residue was used up. A

treatment with bone-black, and a second crystallization from the alcohol, gave a pure substance.

0.2543 gram of substance, dried at 100°, gave 63.4 cc. N at 13°.5 C. and 767.5 mm.

	Theory for $C_6H_4 \diagdown \begin{smallmatrix} NO_2 \\ N_2C_2H_2 \end{smallmatrix}$.	Found.
N	29.47	29.67

p-Nitro-*n*-phenyl-1-2-imidodiazol forms pale-yellow, granular crystals, that melt at 203°–204°. It is difficultly soluble in water, benzene, and alcohol, even in the heat; easily soluble in acetic ester, and hot methyl alcohol. The substance has neutral properties, the introduction of the nitro group having neutralized the slight basic properties of *n*-phenylimidodiazol.

To reduce the nitro group in this compound it was warmed with concentrated hydrochloric acid and tin until complete solution ensued, and the grayish, crystalline tin double salt that separated on cooling, dissolved in hot water, and hydrogen sulphide passed through the warm solution until all the tin was precipitated. On evaporation of the filtrate to dryness in a water-bath, extraction of the residue by water, and addition of an excess of caustic potash to the filtered solution, the new base was precipitated. The yield was not satisfactory, and we found that a somewhat better result was obtained by using stannous chloride as reducer. The substance was warmed with dilute hydrochloric acid, and an amount of stannous chloride slightly in excess of the theory until reduction had taken place. Water was added to the solution, and the liquid treated as already described. The base was obtained pure by two crystallizations from hot water.

I. 0.1520 gram substance, dried at 100° in a vacuum, gave 0.3352 gram CO_2, and 0.0708 gram H_2O.

II. 0.2071 gram substance, dried at 100° in a vacuum, gave 64.5 cc. N at 23°.5 C., and 774.5 mm.

	Theory for $C_6H_4 \diagdown \begin{smallmatrix} NH_2 \\ N_2C_2H_2 \end{smallmatrix}$.	Found.
C	60.00	60.16
H	5.00	5.18
N	35.00	35.60

The substance crystallizes in pearly flakes, that melt at 138°–139°. It is easily soluble in hot water and hot benzene, slightly in hot alcohol and acetic ester. With the ordinary mineral acids it gives salts, which are soluble in water. A small quantity of the base was dissolved in hot water, and, after addition of some alkali, an excess of permanganate added. On working up the solution, as already described for the amidodicarboxylic acid, a crystalline substance and oxalic acid were obtained, but the formation of imidodiazol, which is a liquid and a basic substance, was not noticed.

Addition of Phenylazimide to Phenylpropiolic Ethylester.

In order to ascertain whether the reaction we have described in this paper is applicable to the esters of monobasic acids, we examined the behavior of phenylazimide towards ethyl phenylpropiolate. The addition does not take place as easily as when acetylenecarboxylic ester is used, and the operation is best carried out in a sealed tube at 100°. Five grams of phenylazimide, 7.5 grams ester, and 15 grams dry ether, were heated for sixteen hours, and the tube, when cold, opened under a slight pressure. On standing a short time after opening, the liquid in the tube deposited a crystalline substance, which was separated, washed with benzene, and recrystallized twice from a mixture of three parts benzine and one part benzene. A small amount of addition-product may be obtained by heating the mother-liquor again. The substance gave the following figures for nitrogen :

0.1715 gram substance, dried at 100°, gave 21.8 cc. N at 9.5° C., and 733.5 mm.

	Theory for $C_6H_5-N_3C_2\begin{smallmatrix}C_6H_5\\COOC_2H_5\end{smallmatrix}$.	Found.
N	14.34	14.72

The product crystallizes in needles that melt at 134°–135°, and are freely soluble in benzene and acetic ester in the cold, very soluble in the heat ; but only sparingly soluble in benzine. This addition may proceed in two different ways, forming isomeric products :

$$C_6H_5-N \Big\langle \begin{matrix} N \\ | \\ N \end{matrix} + C_6H_5-C \div C-COOC_2H_5 =$$

I. $C_6H_5-N \Big\langle \begin{matrix} N \div N \\ | \\ H_5C_2OOC-C \div C-C_6H_5 \end{matrix}$

II. $C_6H_5-N \Big\langle \begin{matrix} N \div N \\ | \\ H_5C_6-C \div C-COOC_2H_5 \end{matrix}$
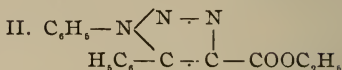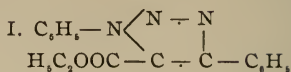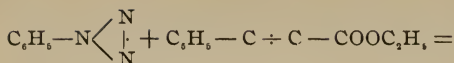
The data for determining with certainty which of these constitutions should be assigned to our substance, are not known, although constitution II. is the more probable. The ester is easily saponified by boiling with alcoholic potash for a short time. On evaporation of the alcohol, and acidifying with chlorhydric acid, the acid is precipitated. By crystallizing twice from dilute alcohol a pure product was obtained.

I. 0.196 gram acid, dried at 100°, gave 0.488 gram CO_2, and 0.080 gram H_2O.

II. 0.220 gram acid, dried at 100°, gave 30 cc. N at 11° C. and 745 mm.

	Theory for $C_6H_5-N_3C_2 \Big\langle \begin{smallmatrix} C_6H_5 \\ COOH \end{smallmatrix}$	Found.
C	67.92	67.85
H	4.15	4.48
N	15.85	15.93

n-Phenylimido-phenyl-1,2-diazolcarboxylic acid is a crystalline, white substance that melts at 183°. It is slightly soluble in water, more easily in alcohol.

A neutral solution of the ammonium salt gives the following reactions :

$BaCl_2$: White, amorphous precipitate.

$MgSO_4$: The mixture remains clear for several minutes, then round groups of needles separate.

$Pb(NO_3)_2$: White, amorphous precipitate.

$CdSO_4$: White, amorphous precipitate.

The silver salt forms a white, amorphous substance, which is difficultly soluble in cold water.

0.559 gram salt, dried in a vacuum, gave 0.161 gram Ag.

	Theory for $C_{14}N_3H_{10}COOAg$.	Found.
Ag	29.03	28.80

The copper salt·is precipitated as an amorphous mass, that soon turns to groups of truncated, slender prisms.

0.2535 gram salt, dried in vacuum, gave 0.0350 gram CuO.

	Theory for $(C_{14}N_3H_{10}COO)_2Cu$.	Found.
Cu	10.70	11.02

Since the fatty monobasic acetylene acids add negative atoms more readily than phenylpropiolic acid, there can be no doubt that the addition of substituted azimides to esters of the acetylenecarboxylic acids to form imidodiazol derivatives is a general reaction.

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CVI. — ON THE OXIDE OF DICHLORMETHOXY-QUINONEDIBENZOYLMETHYLACETAL.[1]

BY C. LORING JACKSON AND H. A. TORREY.

A paper on the acetals derived from substituted quinones published by H. S. Grindley and one of us in 1895, contained a description[2] of a substance made by the action of sulphuric acid on the dichlordimethoxyquinonedibenzoyldimethylacetal, which had the formula, $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$, and which was called then the oxide of dichlordimethoxyhydro-quinone dibenzoate—a name which the better knowledge of its constitution obtained from the work described in this paper makes it necessary for us to change to oxide of dichlor-methoxyquinonedibenzoylmethylacetal.

As it seemed probable that the atom of oxygen in this sub-stance was attached to two of the carbon atoms of the benzol ring, we decided to continue the study of it, and we describe the results of our work in this paper. In the preceding paper nothing had been done with this body beyond establishing its composition and that of the corresponding ethyl compound,

[1] Presented to the American Academy of Arts and Sciences, May 12, 1897. The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by H. A. Torrey.

[2] This JOURNAL, **17**, 644.

and the preparation and partial study of a reduction-product obtained from the ethyl oxide by the action of hydriodic acid.

In taking up again the study of the oxide the first point to be determined was whether the atom of oxygen is attached to one atom of carbon or to two. In the former case the substance must be either a ketone or a phenol. In writing the formula of this substance on the supposition that it is a ketone, it is necessary to assume such improbable intra-molecular transformations that we felt inclined to reject the ketone formula on this ground alone ; and this theoretical deduction was confirmed by the behavior of the substance. Hydroxylamine does not act on the body ; but with phenyl-hydrazine products are obtained, to which we have devoted much attention with little result, because they are so unstable. They seem to resemble the isoamylamine compounds described later, and, if this is the case, tell against a ketone formula for the substance. This evidence, therefore, so far as it goes, is unfavorable to the ketone formula, but not conclusive against it. The action of a hot solution of sodic hydrate on our substance converted it into the sodium salt of chloranilic acid, and this result cannot be brought into harmony with a ketone formula, for in that case the sodic hydrate must have converted the ketone group $C=O$ into a phenol group $C-OH$. The ketone attachment of the oxygen must, therefore, be rejected.

We have not succeeded in constructing any formula for our substance with the oxygen present in a hydroxyl group, as this would give 7 substituting radicals to be arranged upon the benzol ring ; and we may add that the existence of a hydroxyl group is inadmissible on experimental grounds, since cold sodic hydrate has no action upon the substance.

After we had thus proved that the oxygen is not attached to a single atom of carbon, a molecular weight determination was made, which showed that the body was derived from only one molecule of the substituted quinone. We next considered the different ways in which the atom of oxygen could be attached to 2 atoms of carbon, and this led to 4 possible formulas for the substance :

I.

COC_6H_5
|
O
|

CH_3O / Cl
O
Cl / OCH_3
|
O
|
COC_6H_5

II.

CH_3-O O-COC_6H_5
Cl
O
Cl
CH_3O O-COC_6H_5

III.

O O-COC_6H_5
Cl
Cl OCH_3
CH_3O O-COC_6H_5

IV.

O-COC_6H_5
CH_3O Cl O
Cl
CH_3O O-COC_6H_5
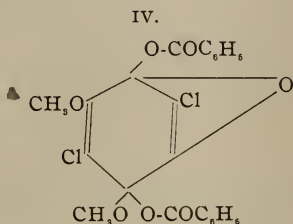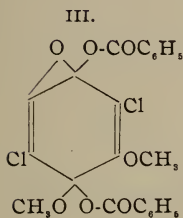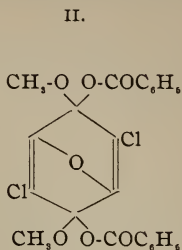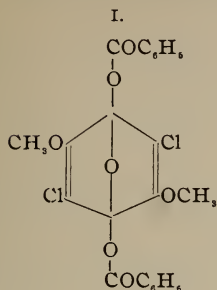
In formulas I. and II. the attachment is to two atoms of carbon in the para position, which in I. are the quinone atoms of carbon, in II. those which are attached to the hydroxyls in chloranilic acid. Formula III. represents the oxygen attached to 2 atoms of carbon in the ortho position; and formula IV. shows a meta attachment. Of the formulas we considered I. or II. the most probable, and devoted ourselves at first to the study of these.

The conversion of the substance into chloranilic acid by the action of hot sodic hydrate can be easily explained by all four of these formulas, and therefore gives no aid in distinguishing between them.

Isoamylamine converts the oxide into the isoamylamine salt of oxydichlorisoamylamidoquinone, which has the following formula:
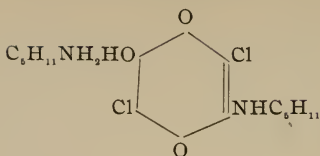
In forming this substance from a body having formula I., it is necessary that the two methoxy groups should be acted on differently by the isoamylamine, since one of them is replaced by the isoamylamido group ($C_5H_{11}NH$), and the other converted into the phenol salt group ($C_5H_{11}NH_2HO$). Such an action would be highly improbable theoretically, as these two methoxy groups are symmetrically disposed in this formula; and it is proved to be impossible by our study of the action of isoamylamine on the similarly constituted dichlordimethoxyquinonedimethyldibenzoylacetal,

$$C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2,$$

which was converted by it into dichlordiisoamylamidoquinone, $C_6Cl_2(NHC_5H_{11})_2O_2$. Formula I., therefore, is not in harmony with these observations, and must be rejected. Formulas II., III., and IV. can be easily brought into harmony with the results of the experiments with isoamylamine, as will be shown later.

Sodic methylate converted the oxide into the sodium salt of the dichlordimethoxyquinonedimethylhemiacetal, which has the following formula:
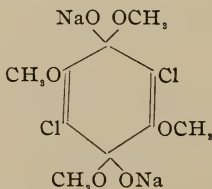
In deriving this compound from a substance having formula II., the atom of oxygen must take up a molecule of sodic

methylate, thus producing the intermediate body of these formulas :[1]

Oxide.   Intermediate body.   Hemiacetal.
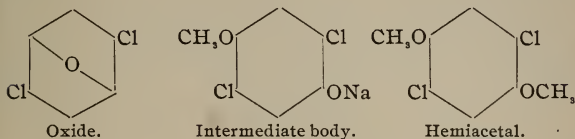
And then we must assume that the ONa of this body is converted into the OCH_3 of the hemiacetal by sodic methylate, an assumption which cannot be justified by any analogy, so that formula II. must also be rejected.[2]

There remain only formulas III. and IV., the unsymmetrical structure of which made us at first think them highly improbable ; as a matter of fact, however, both of them explain in a satisfactory manner all the observations. This we will show only with formula III., since formula IV. would behave in a similar manner in every case.

The conversion of the oxide into chloranilic acid by sodic hydrate would take place in three stages ; first, the addition of 1 molecule of sodic hydrate to the atom of oxygen, thus :

Oxide.   Intermediate product.   Chloranilic Acid.
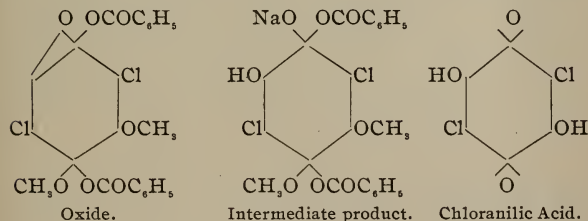
second, the saponification of the acetal groups to the quinone ;

[1] In these formulas the radicals in the quinone positions have been left out for the sake of simplicity. They offer no difficulties, as will be shown later.

[2] It is perhaps worth while to state that the conversion of the hypothetical intermediate body into the hemiacetal could be brought about by splitting off sodic benzoate, thus forming a new oxide, which afterward might react with the sodic methylate ; but, as this new oxide must have the conformation of either formula III. or IV., it does not seem worth while to bring this strained hypothesis forward as a support for formula II.

and third, the saponification of the methoxy group to a hydroxyl.[1]

The formation of the isoamylamine salt of oxydichloriso-amylamidoquinone by the action of isoamylamine on the oxide would begin by the addition of one molecule of isoamylamine, forming the intermediate product, which would then

Oxide.   Intermediate product.   Product.
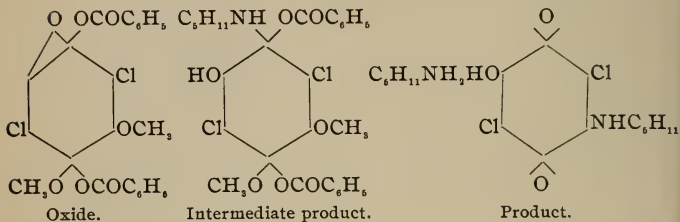
be followed by the conversion of the acetal groups to the quinone, the replacement of the methoxy group by the isoamylamido group $C_6H_{11}NH$, and the addition of a molecule of isoamylamine to the hydroxyl. The two steps in this conversion which might be regarded as doubtful are the conversion of the acetal to the quinone by isoamylamine, and the replacement of the methoxy by the isoamylamido group. Fortunately, we have been able to remove all doubt about both these steps by acting on the dichlordimethoxy-quinonedimethyldibenzoylacetal,

$$C_6Cl_2(CH_3O)_2(CH_3O)_2(OCOC_6H_5)_2,$$

with isoamylamine, when it was converted into dichlordiiso-amylamidoquinone, $C_6Cl_2(C_6H_{11}NH)_2O_2$.

The formation of the sodium salt of the dimethylhemiacetal by the action of sodic methylate on the oxide is explained in a similar way:

[1] That such methoxy groups on a quinone ring are saponified by sodic hydrate has been shown by the experiments of H. S. Grindley and one of us. (This JOURNAL, **17**, 606.) In this respect they resemble those in picric ether or trinitrophloroglucine ether much more than those in anisol.

O OCOC₆H₅	NaO OCOC₆H₅	NaO OCH₃

Oxide.   Addition product.   Hemiacetal.
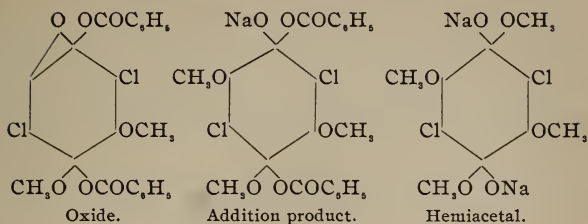
The formation of the intermediate addition-product being fol-
lowed by conversion into a quinone, which then takes up 2
molecules of sodic methylate to form the hemiacetal.

The only other derivative of the oxide known is the reduc-
tion-product[1] obtained by Grindley and one of us by the ac-
tion of hydriodic acid. This substance gave upon analysis
the formula $C_6Cl_2OC_2H_5OH(OCOC_6H_5)_2$, but has not yet been
studied sufficiently to determine its constitution with cer-
tainty. We shall therefore content ourselves with saying that
a substance with the formula given above could be easily de-
rived from the oxide with the ortho attachment by the action
of hydriodic acid.

In the foregoing discussion of the formulas of the oxide, the
arguments were based in large part among the product ob-
tained from it by the action of isoamylamine, and it is neces-
sary, therefore, here to give our proofs of the constitution of
this body. Its analysis led to the formula

$$C_6Cl_2(C_5H_{11}NH)(C_5H_{11}NH_2HO)O_2,$$
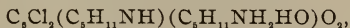
which represents an isoamylamine salt of a phenol, and this
view was confirmed by the following observations: sodic
hydrate set free isoamylamine from it; with hydrochloric acid a
substance was obtained of the formula $C_6Cl_2(C_5H_{11}NH)HOO_2$,
and melting at 188°; argentic nitrate converted it into

$$C_6Cl_2(C_5H_{11}NH)AgOO_2,$$
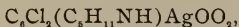
and we have also made the corresponding barium salt. That it
was a quinone was shown by its dark color and its conversion
into a colorless product by reduction. For the sake of com-

[1] This JOURNAL, **17**, 641.

parison with this body we made the dichlordiisoamylamido-
quinone, $C_6Cl_2(C_5H_{11}NH)_2O_2$, by the action of isoamylamine
on chloranil ; it melted at 224° to 225° ; and also the isoamyl-
amine salt of chloranilic acid, $C_6Cl_2(OHH_3NC_5H_{11})_2O_2$, both of
which differed entirely in properties from the product made
from the oxide.

The oxide when treated with diisoamylamine gave a com-
pound corresponding to that from isoamylamine,

$$C_6Cl_2(C_5H_{11})_2N(C_5H_{11})_2NHHOO_2,$$
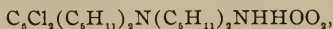
melting at 168°–169°. With chloranil, diisoamylamine gave

$$C_6Cl_2((C_5H_{11})_2N)_2O_2.$$

In looking for actions analogous to those just described, we
are obliged to resort to the fat series, as no oxide similar to
ours is known in the aromatic series, the nearest approach to
it being cineol according to the formula ascribed to it by
Brühl, in which, however, the oxygen spans the benzol ring
in the para position. In the fat series ethylene oxide shows
a structure similar to that of our oxide, as its atom of oxygen
is attached to two adjacent atoms of carbon ; and in its behavior
with various reagents we find a marked similarity to the reac-
tions of our oxide. Thus its conversion into glycol by the
action of water corresponds to the formation of chloranilic
acid by sodic hydrate, and with ammonia the ethylene oxide
gives, among other products, an amino-alcohol,

$$HOCH_2CH_2NH_2,$$
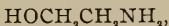
analogous to the intermediate product which must be formed
by the action of isoamylamine on our oxide. On the other
hand, we have not been able to find any case in which a fat
oxide belonging to another than the α series shows these re-
actions, and this, so far as it goes, throws the balance in favor
of adopting the ortho attachment of the oxygen (formula III.)
rather than the meta attachment (formula IV.) in our oxide.

The decision between formula III. (with the ortho attach-
ment) and formula IV. (with the meta attachment) could not
be founded on any study of the derivatives of the oxide, as
both formulas would give the same products when the oxygen

bond was opened. We accordingly tried to solve the problem by the study of analogous substances, as follows : we exposed to the action of boiling sulphuric acid resorcine as an example of a substance with meta hydroxyls, and pyrocatechine (or some of its derivatives) as a substance with ortho hydroxyls, in the hope of obtaining an oxide similar to the one we have been studying, but in neither case was an oxide of this class formed. Resorcine under the action of boiling dilute sulphuric acid gave a body which we recognized by its properties as resorcine ether, formed by the union of 2 molecules of resorcine. The experiments with pyrocatechine and its derivatives, when the substance underwent any change, gave colored products, which were probably formed from a quinone. These experiments, therefore, threw no light upon the question.

From the discussion given above it appears that we cannot decide with certainty whether the oxygen in our oxide is in the ortho or meta position ; we are of the opinion, however, that it has the ortho attachment, not only from the analogy between our oxide and ethylene oxide pointed out above, but also from the fact that the formation of anhydrides and similar couplings by two radicals in the meta position to each other are unknown, whereas these actions are among the most familiar characteristics of the ortho series.

We also describe tetrabromguaiacol, melting at 162°–163°, and tribromveratrol, melting at 86°–87°, which were made in connection with our work on the action of sulphuric acid on derivatives of pyrocatechine.

When we first undertook this work we devoted a great deal of time to the preparation of mixed acetals like the dichlordiethoxyquinonedimethyldibenzoylacetal, as we hoped by the saponification of these substances to be able to determine which of the formulas of the oxide was correct ; but these experiments led to no satisfactory result, as the action of sodic methylate on dichlordiethoxyquinone, or of sodic ethylate on dichlordimethoxyquinone, produced mixtures from which the desired compounds could not be isolated. This is not surprising, as we found subsequently that the ethoxy groups could be replaced by methoxy groups, or the reverse, when

one of our compounds was treated with the sodic alcoholate containing the radical, which was not already attached to its quinone ring.[1]

The acetyl acetals corresponding to the benzoyl acetals have also been made by us, and have the following melting-points :

$C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOCH_3)_2$, melting-point $177°-178°$.

$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOCH_3)_2$, melting-point $120°-121°$.

We also describe some experiments on the action of sodic alcoholates on quinone itself and on chloranil, which led to substances probably similar to the colored compounds obtained from nitro aromatic bodies by the action of sodic alcoholates by Lobry de Bruyn,[2] Victor Meyer,[3] and Ittner and one of us.[4] These experiments were abandoned after some progress had been made on account of the work of Astre[5] in the same field, and are described here only because they cannot be brought into harmony with the theory advanced by Astre to account for these substances. The discussion of this question will be found in the experimental part.

We also observed that an alkaline solution of sodic chloranilate was converted into iodoform by treatment with iodine.

Experimental Part.

Preparation of the Oxide of Dichlormethoxyquinonedibenzoylmethylacetal, $C_6Cl_2OCH_3O(CO_2C_6H_5)_2OCH_3$.

This preparation was carried on essentially in the manner described by Grindley and one of us in a previous paper,[6] but we think it best to describe the process again here, as in that paper it is not given continuously, but scattered through different paragraphs, and also because we have introduced a few improvements in the details.

To convert chloranil into dichlordiphenoxyquinone 50 grams of chloranil, previously converted to a fine powder by reduction to tetrachlorhydroquinone by sulphurous acid followed by

[1] Compare Gattermann and Ritschke, Ber. d. chem. Ges., **23**, 1738 (1890).

[2] Rec. Trav. Chim. Pays-Bas, **14**, 89.   [3] Ber. d. chem. Ges., **27**, 3153.

[4] This JOURNAL, **19**, 199.   [5] Compt. rend., **121**, 326, 530.

[6] This JOURNAL, **17**, 600.

oxidation with nitric acid,[1] were treated with a strong aqueous solution of potassic phenylate made from 50 grams of phenol and 25 grams of potassic hydrate. The product was washed thoroughly with water, then with alcohol, and finally with benzol or ether. It was not recrystallized.

The dichlordiphenoxyquinone was then converted into the dichlordimethoxydimethylhemiacetal by adding 20 grams of it in small portions at a time with constant agitation to the sodic methylate made from 5 grams of metallic sodium and 120 cc. of methyl alcohol. It was found best to carry on this reaction in a flask. The mixture was then warmed on the water-bath, and afterward allowed to stand for a short time to permit the separation of the sodium salt of the hemiacetal, which was sometimes hastened by the addition of a little ether. The salt collected on a filter was washed with ether and with a very little alcohol, or better a mixture of alcohol and ether.

The dibenzoylacetal was next made by treating 25 grams of the dry salt suspended in a small quantity of methyl alcohol with 22 grams of benzoyl chloride. The reaction was completed by warming the mixture for a short time on the water-bath. The product usually contained, in addition to the colorless dibenzoylacetal, a red substance, probably dichlordimethoxyquinone, which was most easily removed by treatment with warm sodic hydrate, as this reagent converted the red substance into sodic chloranilate, but did not act on the acetal. The chloranilate was then washed with hot water, leaving the acetal pure enough for our purposes.

The dry acetal was next saponified by heating it for fifteen or twenty minutes in a flask with a return-condenser with sulphuric acid of specific gravity 1.44. The contents of the flask were then allowed to cool, and after the addition of a little water the solid product was filtered out, and washed with hot water to remove the chloranilic acid always formed in the reaction. The white oxide left was then purified by one or two recrystallizations from chloroform and alcohol. The yield of oxide was a little under 80 per cent. of the amount which should be obtained from the acetal.

[1] This preliminary treatment is essential to the success of the process. We have not succeeded in getting a sufficiently fine powder by mechanical means.

The processes which are carried on in this preparation are represented by the following equations:

$$C_6Cl_4O_2 + 2NaOC_6H_5 = C_6Cl_2(OC_6H_5)_2O_2 + 2NaCl.$$
$$C_6Cl_2(OC_6H_5)_2O_2 + 4NaOCH_3 =$$
$$C_6Cl_2(OCH_3)_2(ONa)_2(OCH_3)_2 + 2NaOC_6H_5.$$
$$C_6Cl_2(OCH_3)_2(ONa)_2(OCH_3)_2 + 2C_6H_5COCl =$$
$$2NaCl + C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2(OCH_3)_2.$$
$$C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2(OCH_3)_2 + H_2O =$$
$$C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3 + 2CH_3OH.$$
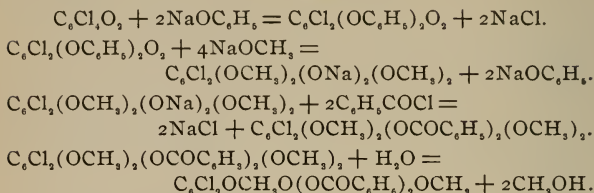
Determination of the Molecular Weight of the Oxide.

This determination was made to find out whether the oxide was derived from one or more molecules of the benzoylacetal. The boiling-point method of Beckmann was used with benzol as the solvent, and the following results were obtained:

Solvent.	Substance.	Δ.	M.
17.08	0.4315	0.138°	489
17.05	0.6761	0.228°	465
17.02	0.9787	0.328°	468
		Mean,	474

The temperature error did not exceed 3 in the last decimal place.

Calculated molecular weight for $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$.	Found. Mean.
463	474

These results show that the oxygen atom does not bind together 2 benzol rings.

Action of Sodic Hydrate on the Oxide,
$$C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3.$$

The oxide did not dissolve in a cold solution of sodic hydrate, but when the two substances were allowed to stand together for twenty hours, it was found that a small quantity of sodic chloranilate had separated out.

If on the other hand, the oxide was boiled with sodic hydrate, it was decomposed rapidly even when a dilute solution was used. 1.5 grams of the oxide were boiled for half an

hour with a solution of 5 grams of sodic hydrate in 60 cc. of water; at the end of this time the oxide had disappeared completely, and the liquid had taken on a dark purple color. It was filtered while still hot, and the filtrate on cooling deposited crystals, which looked like sodic chloranilate. To determine their composition they were collected on a filter, and, after washing with alcohol and a little water, recrystallized from hot water. The crystals were then dried over sulphuric acid, and finally at $110°$–$120°$, when an analysis gave the following result:

0.1707 gram of the salt gave 0.0949 gram of sodic sulphate.

	Calculated for $C_6Cl_2(ONa)_2O_2$.	Found.
Sodium	18.18	18.02

The product was therefore sodic chloranilate.

Action of Sodic Methylate on the Methyl Oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$.

One gram of the oxide was added to a solution of sodic methylate made by the action of 0.2 gram of metallic sodium on 10 cc. of methyl alcohol. After heating the mixture for a short time on the water-bath the liquid became slightly yellow, and the oxide went into solution, but soon after a white substance was deposited, the quantity of which increased as the liquid cooled; at the same time the odor of methyl benzoate was observed. The product of the reaction was allowed to stand at ordinary temperatures for half an hour, after which the white precipitate was collected on a filter, and washed at first with methyl alcohol, in which it is only slightly soluble, and finally with ether. The washed precipitate was then dissolved in water, and the solution, after it had been filtered, acidified with dilute hydrochloric acid. The white flocculent precipitate formed by the acid was washed thoroughly with water, alcohol, and ether; and next redissolved in sodic hydrate, filtered, and reprecipitated with dilute hydrochloric acid. These solutions and reprecipitations were repeated several times until the precipitate was perfectly white.

The amorphous white substance thus obtained was very similar in appearance to a hemiacetal. It was dried and analyzed with the following result:

0.1368 gram of the substance gave, by the method of Carius, 0.1300 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2$.	Found.
Chlorine	23.59	23.48

This analysis indicates that the substance is the dichlordimethoxyquinonedimethylhemiacetal, and this view of its composition is confirmed by the following experiment. A small quantity of the substance was heated with dilute hydrochloric acid, when a red crystalline body was obtained melting in the crude state at 140°, after crystallization at 141°. This must therefore have been the dichlordimethoxyquinone whose melting-point is 141°–142°.

The hemiacetal could be formed from the oxide by the following reactions :

$$C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3 + NaOCH_3 =$$
$$C_6Cl_2(OCH_3)_2ONa(OCOC_6H_5)_2OCH_3 =$$
$$C_6H_5COONa + C_6H_5COOCH_3 + C_6Cl_2(OCH_3)_2O_2.$$
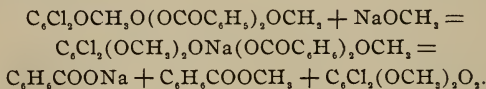
An odor of methyl benzoate was observed, as already stated.

$$C_6Cl_2(OCH_3)_2O_2 + 2NaOCH_3 =$$
$$C_6Cl_2(OCH_3)_2(ONa)_2(OCH_3)_2.$$
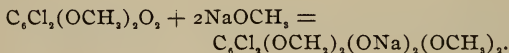
Action of Sodic Methylate on the Ethyl Oxide,
$$C_6Cl_2(OC_2H_5)O(OCOC_6H_5)_2OC_2H_5.$$
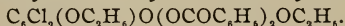
One gram of the ethyl oxide was added to a solution of sodic methylate made by the action of 0.2 gram of sodium on 12 cc. of methyl alcohol. The oxide went into solution at once, but after the solution had been heated on the steambath for a short time a white precipitate was thrown down, the amount of which was increased by the addition of ether. After purification by alternate precipitation by hydrochloric acid, and solution in sodic hydrate, as described in the preceding section, the substance was dried in a desiccator, and analyzed with the following result :

0.1527 gram of the free hemiacetal gave, by the method of Carius, 0.1456 gram of argentic chloride.

	$C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2$.	Found.
Chlorine	23.59	23.58

As the mixed ethyl methylhemiacetal, which would be expected here, contains 21.58 per cent. of chlorine, there can be no doubt that the product was the dimethylhemiacetal; and this view was confirmed by the following experiment: A small quantity of the substance was heated with dilute hydrochloric acid, when a red solid was formed which melted at 140°, and therefore was the dichlordimethoxyquinone. From these observations it follows that the behavior of the ethyl oxide with sodic methylate is the same as that of the methyl oxide, except that, in addition to the formation of the hemiacetal, the ethoxy groups have been replaced by methoxy groups.

After the work just described had shown that ethoxy groups in the ethyl oxide could be replaced by methoxy groups under the influence of sodic methylate, the following experiment was tried to see whether a similar change could be produced with the dichlordiethoxyquinone: 0.7 gram of this substance was treated with a solution of the sodic methylate made from 0.2 gram of sodium and 5 cc. of methyl alcohol; the hemiacetal formed was decomposed with dilute hydrochloric acid, and the red quinone obtained recrystallized from alcohol, and then from benzol, when it melted at 139°, showing that it was dichlordimethoxyquinone, and therefore that the methoxy groups had replaced the ethoxy groups in this case also, as was to be expected.

We next tried an experiment to see whether the reverse change could be brought about. One gram of the methyl oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$, was treated with a solution of sodic ethylate, and the hemiacetal formed decomposed with hydrochloric acid, when the crude quinone thus obtained melted at 100°–105°, and recrystallization did not raise the melting-point above 105°; it is, therefore, dichlordiethoxyquinone, which melts at 104°–105°, and the ethoxy group has replaced the methoxy group. These experiments make it probable that any alcohol radical can be replaced by any other in these substituted quinones, if the substance is

treated with the proper sodic alcoholate,[1] and therefore that
the isolation of mixed hemiacetals containing one radical on the
ring and another in the acetal part of the molecule would be
a matter of great difficulty.　　These experiments were in fact
undertaken to explain the failure of our work on such mixed
hemiacetals and acetals, which we had tried to prepare, because
we hoped that the conversion of them into the corresponding
oxides would throw some light on the constitution of these
latter bodies.　Our attempts to make the dimethoxyquinone-
diethyldibenzoylacetal led to the diethoxydiethyl body as the
principal product, but probably a small quantity of the mixed
acetal was also formed, as the crude product began to melt at
130°, and it was only after many crystallizations that the pure
diethoxydiethylacetal melting at 170° could be obtained.

Action of Isoamylamine on the Oxide,
$C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3.$

Three grams of the oxide were dissolved in hot benzol, and
4.5 grams of free isoamylamine were added with constant
stirring.　A reaction took place at once with the formation of
a yellow precipitate so abundant that the contents of the
beaker became almost solid.　As this yellow substance is very
unstable, we devoted our attention at first to the product of
its decomposition, which was more easily obtained and purified.
To bring about the decomposition the mixture was heated
gently, when the yellow color changed to a purplish red, and
the greater part of the solid went into solution, but was de-
posited as the benzol cooled.　The purplish-red solid thus
obtained was washed with benzol, and then with water, after
which it was purified by recrystallization from hot benzol, to
which a very little methyl alcohol had been added.　It was
then dried at 100° and analyzed with the following results:

I.　0.1089 gram of the substance gave, by combustion, 0.2085
gram of carbonic dioxide and 0.0715 gram of water.

II.　0.1147 gram of the substance gave, by the method of
Carius, 0.0931 gram of argentic chloride.

1 Replacements similar to these have been observed with other classes of bodies
by Friedel and Crafts, Ann. Chem. (Liebig), **133**, 208; Israel, *Ibid*, **231**, 220; Isbert,
Ibid, **234**, 160; Peters, *Ibid*, **257**, 353; Purdie, Ber. d. chem. Ges., **20**, 1554; Bertoni,
Gaz. Chim., **12**, 435; **15**, 361; and Gattermann and Ritschke, Ber. d. chem. Ges., **23**,
1738 (1890).

III. 0.1216 gram of the substance gave 0.0969 gram of argentic chloride.

	Calculated for $C_6Cl_2C_5H_{11}NHONH_2C_5H_{11}O_2$.	I.	Found. II.	III.
Carbon	52.60	52.22	....	....
Hydrogen	7.19	7.29	....	....
Chlorine	19.45	....	20.06	19.71

These results show that the substance is the isoamylamine salt of the dichlorisoamylamidoxyquinone. The formation of such a body from the oxide can be explained by the following reactions :[1] In the first place, the addition of 1 molecule of isoamylamine to the atom of oxygen forming

$$C_6Cl_2OCH_3OH(C_5H_{11}NH)(OCOC_6H_5)_2OCH_3 ;$$

next, the replacement of the methoxy group by an isoamyl-amido group, and the addition of a molecule of isoamylamine to the hydroxyl giving a complex substance, which must have had this formula :

$$C_6Cl_2(C_5H_{11}NH)(OHNH_2C_5H_{11})C_5H_{11}NH(OCOC_6H_5)_2OCH_3.$$
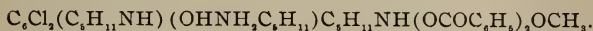
This would finally be decomposed by the removal of benz-isoamylamide and methyl benzoate leaving the body ana-lyzed,

$$C_6Cl_2C_5H_{11}NHOHC_5H_{11}NH_2O_2.$$
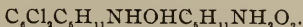
That the methoxy group can be replaced by the isoamyl-amido radical and the substituted acetal saponified to the quinone under these conditions will be proved by some ex-periments described later in this paper.

Properties of the Isoamylamine Salt of Dichlorisoamylamid-oxyquinone, $C_6Cl_2(C_5H_{11}NH)(OHNH_2C_5H_{11})O_2$.—This sub-stance, when crystallized from a mixture of benzol and methyl alcohol, appears in purplish-red needles, which, when exam-ined with the microscope, are seen to be long, very slender, spindle-shaped plates or flattened needles of a pale-purple color. When heated it decomposes into the free phenol melting at its usual temperature, 188°, and isoamylamine, which could be seen coating the upper parts of the melting-

[1] These reactions are arranged in the order which we think will be most easily understood. We do not mean to imply that they took place in this order ; in fact, our work on the yellow product seems to indicate that they did not.

tube, and was recognized by its odor. It is easily soluble in methyl or ethyl alcohol; soluble in acetone, or acetate of ethyl; slightly soluble in cold benzol, or chloroform, more soluble in either of these solvents when hot; insoluble in ether, ligroïn, carbonic disulphide, or water; glacial acetic acid dissolves it, but nothing is precipitated from this solution by the addition of water. All of its solutions show a purple color. The best solvent for it is a mixture of benzol and a little methyl alcohol. Dilute hydrochloric acid, or nitric acid, converts it into a black powder. If a strong acid is used, a red solution is formed, from which water precipitates the black substance. The most convenient way of obtaining the black body is by adding dilute hydrochloric acid to an alcoholic solution of the salt, when it is precipitated. It is the free phenol, $C_6Cl_2(C_5H_{11}NH)OHO_2$, which is described later in this paper. An aqueous solution of sodic hydrate does not dissolve the substance, but, if the alkali is added to an alcoholic solution of the salt, a light-colored compound is precipitated, and at the same time the odor of an amine is observed; heavy white fumes are produced, when hydrochloric acid vapors are brought near the vessel containing this mixture. The precipitate is therefore probably the sodium salt, but it was not thought worth while to study it. Baric chloride gives a violet precipitate, argentic nitrate a red gelatinous precipitate, when added to an alcoholic solution of the salt. These precipitates were more carefully studied in order to characterize the substance more thoroughly.

Silver Salt of Dichlorisoamylamidoxyquinone, $C_6Cl_2(C_5H_{11}NH)OAgO_2.2H_2O.$

This salt was prepared by adding to a dilute alcoholic solution of the isoamylamine salt an aqueous solution of argentic nitrate in excess. After stirring the solution for some time a mass of olive-gray needles separated, which were collected on a filter, washed very thoroughly with water, and with a mixture of alcohol and water, sucked dry on the filter-pump, and then dried in a desiccator over sulphuric acid to a constant weight. The analysis of the salt gave the following results:

0.1387 gram of the salt, dried in a desiccator, lost 0.0124 gram of water when heated to 105°–110°.

	Calculated for $C_6Cl_2(C_5H_{11}NH)OAgO_2.2H_2O$.	Found.
Water	8.58	8.94

The amount of silver in the salt dried at 105°–110° was determined by heating it in a sealed tube with nitric acid (specific gravity 1.5) and weighing the argentic chloride formed.

I. 0.1223 gram of the substance gave 0.0459 gram of argentic chloride.

II. 0.1866 gram of the substance gave, by the method of Carius (with an excess of argentic nitrate), 0.1425 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_5H_{11}NH)OAgO_2$.	I.	II.
		Found.	Found.
Silver	28.05	28.18	....
Chlorine	18.44	....	18.88

Properties of the Silver Salt.—If in making this salt the argentic nitrate is added slowly to a cold dilute solution of the isoamylamine salt, and the separation takes place slowly, the salt is obtained in olive-gray needles, which contain 2 molecules of water of crystallization, as shown by the analysis given above. These needles, when heated to 110°, lose the water of crystallization, and turn red. If, on the other hand, the solution of argentic nitrate is added to a warm concentrated solution of the isoamylamine salt, a red gelatinous precipitate is obtained, which looks very much like currant jelly, and to judge from its color consists of the anhydrous salt. The red gelatinous mass showed a tendency to pass over into the gray crystalline form ; and the red amorphous body could be obtained from the gray needles by dissolving them in a hot mixture of alcohol and water, and cooling rapidly. The crystallized salt is very slightly soluble in cold water, more so in hot ; slightly soluble in alcohol. The red amorphous form is insoluble in either water or alcohol.

The colorless filtrate from the olive-gray crystals obtained in the preparation of the silver salt was treated with sodic hydrate, when a strong smell of isoamylamine was observed,

showing that the atom of silver had replaced the molecule of isoamylamine in the original salt, as was to be expected.

Barium Salt of Dichlorisoamylamidoxyquinone,
$[C_6Cl_2(C_5H_{11}NH)OO_2]_2Ba.2H_2O.$

This salt was prepared by adding a dilute solution of baric chloride to the isoamylamine salt, dissolved in cold alcohol. The purplish precipitate was collected on a filter, and washed first with alcohol, and afterward with water, until the wash-water gave no test for a chloride. It was then dried *in vacuo* over calcic chloride, and analyzed with the following results:

0.2063 gram of the salt dried *in vacuo* lost 0.0100 gram of water when heated to 110°.

	Calculated for $[C_6Cl_2(C_5H_{11}NH)OO_2]_2Ba.2H_2O.$	Found.
Water	4.95	4.85

0.1958 gram of the salt dried at 110° gave 0.0641 gram of baric sulphate.

	Calculated for $[C_6Cl_2(C_5H_{11}NH)OO_2]_2Ba.$	Found.
Barium	19.83	19.25

Properties of the Barium Salt.—It consists of crystalline plates of a violet color, which are slightly soluble in cold water, more soluble in hot, but insoluble in alcohol. A dilute solution of the salt gives the black, free oxyquinone on addition of hydrochloric acid.

Dichlorisoamylamidoxyquinone, $C_6Cl_2(C_5H_{11}NH)OHO_2.$

This substance is formed whenever one of its salts is treated with dilute hydrochloric acid. It was prepared for analysis by adding dilute hydrochloric acid to a solution of the purple isoamylamine salt in warm alcohol; the black precipitate thus obtained was washed thoroughly with water, and then crystallized from hot benzol, until it showed the constant melting-point 188°, when it was dried at 100°, and analyzed with the following results:

0.1756 gram of the substance gave, by the method of Carius, 0.1832 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_5H_{11}NH)OHO_2$.	Found.
Chlorine	25.54	25.80

Properties of Dichlorisoamylamidoxyquinone.—The substance forms bronze-black, flattened needles, or long plates. When crystallized from hot alcohol and examined with the microscope, rhombic plates are sometimes observed, which are more usually united into short and broad plates looking like an hour glass ; these crystals have a brownish-yellow color, but look black when in thick layers, as, for instance, when two plates overlap, the portions in contact with each other look black, while the other parts of both plates are brownish-yellow, thus giving a very characteristic effect. As the crystallization continues, the hour-glass forms develop into the long plates mentioned at first. It melts at 188° ; it is soluble in methyl or ethyl alcohol, benzol, chloroform, ether, or acetone ; slightly soluble in ligroïn ; very slightly soluble in carbonic disulphide. Benzol is the best solvent for it. Its solutions show a purple color. Strong sulphuric acid dissolves it with a purple color, but the original substance is precipitated from this solution by dilution with water. Sodic hydrate dissolves it, forming a purple solution, from which acids throw down the unaltered substance. The properties of the substance, therefore, confirm the inference drawn from its preparation and analysis, that this is the free oxyquinone.

Yellow Product of the Action of Isoamylamine on the Oxide.

In the description of the action of isoamylamine on the oxide it was stated that a yellow substance was formed at first, which was converted by heating the mixture into the purple isoamylamine salt of the dichlorisoamylamidoxyquinone. It would have been interesting to determine the composition of this intermediate product between the salt and the oxide, but unfortunately it was so unstable, and its properties rendered its purification so doubtful, that we can make no certain statement in regard to it.

It was prepared by dissolving 0.5 gram of the oxide,

$$C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3,$$

in a large quantity of benzol, and adding with continual stir-

ring 0.6 gram of isoamylamine. The solution immediately
turned yellow, and after standing for a minute or two sud-
denly began to coagulate, and finally solidified entirely into a
yellow, gelatinous mass with a slight, greenish fluorescence.
It was washed on a filter with benzol, until the filtrate, which
was red at first, became colorless, and was then dried on a
porous plate, but as it darkened somewhat, it was washed
again with chloroform and alcohol, until it was yellow
throughout. After drying *in vacuo* an analysis was made,
which gave 16.66 per cent. of chlorine. This is not far re-
moved from 15.93, the percentage of chlorine in the not im-
probable intermediate compound,

$$C_6Cl_2CH_8O(OHNH_2C_5H_{11})O(OCOC_5H_5)OCH_8,$$

in which one of the acetal groups has been saponified to a
quinone oxygen. We did not attempt to get more analyses
of this substance, because, owing to its instability and amor-
phous character, we did not feel that much confidence could
be placed in them, and therefore preferred to devote our time
to work which had a more immediate bearing on the nature
of the oxide, and also promised to give more trustworthy re-
sults.

Action of Isoamylamine on Chloranil. Dichlordiisoamylamido-quinone, $C_6Cl_2(C_5H_{11}NH)_2O_2$.

The work described in this and the two following sections
of the paper was undertaken to obtain bodies closely related
to our isoamylamine salt of dichlorisoamylamidoxyquinone,
the study of which might throw some light on the formation
of that body.

Two grams of chloranil were dissolved in hot benzol, and
heated with two grams of isoamylamine with constant stir-
ring. At first a green coloration was noticed, similar to that
obtained by the action of sodic alcoholates on chloranil, but
on longer heating of the mixture this green color gave place
to a purple, and, on cooling, beautiful purple plates separated
from the solution. The substance was washed thoroughly
with alcohol to remove a white impurity, probably the chlo-
ride of isoamylamine, which had separated with it, and then

recrystallized from benzol until it showed the constant melt-ing-point 224°–225°, when it was dried at 100°, and analyzed with the following result :

0.1786 gram of the substance gave, by the method of Carius, 0.1500 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_5H_{11}NH)_2O_2$.	Found.
Chlorine	20.46	20.76

Properties of Dichlordiisoamylamidoquinone.—The substance crystallizes in long plates or flattened needles terminated by a single plane at a not very oblique angle to the sides. The color is a dark red, and the crystals often show a marked pur-ple iridescence when separating from solution. It melts at 224°–225°. It is slightly soluble in cold benzol, more freely in hot ; almost insoluble in alcohol ; insoluble in water. The best solvent for it is benzol. Strong hydrochloric acid has no apparent action on it ; strong sulphuric acid dissolves it, but the original red body is precipitated on the addition of water.

Action of Isoamylamine on Dichlordimethoxyquinonedimethyldi-benzoylacetal.

To study this action 0.7 gram of the acetal was dissolved in hot benzol, mixed with 1.1 grams of isoamylamine, and the mixture heated to boiling on the steam-bath. On cooling, crystals were deposited similar in appearance to those ob-tained by acting on chloranil with isoamylamine. After crys-tallization from benzol they melted at 224°–225°, and there-fore were the dichlordiisoamylamidoquinone, with which the substance also agreed in its other properties. Dichlordimeth-oxyquinone also gives this same product, when treated with isoamylamine.

These experiments show that the methoxy radical in these substituted quinones can be replaced by the isoamylamido group, when the quinone is heated with isoamylamine, and also that isoamylamine can convert a benzoylmethyl-acetal into the corresponding quinone, two points which are of great importance in interpreting the transformations of the oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$, under the influence of isoamylamine.

Isoamylamine Salt of Chloranilic Acid,
$$C_6Cl_2(OHNH_2C_5H_{11})_2O_2.$$

This salt was made by dissolving a small quantity of chloranilic acid in warm alcohol, and adding a slight excess of isoamylamine ; the salt appeared as an abundant, purplish-red precipitate, which was purified by washing it with benzol, alcohol, and water. It was dried at 110°, and gave the following results on analysis :

I. 0.1307 gram of the salt gave, by the method of Carius, 0.0992 gram of argentic chloride.

II. 0.2208 gram of the salt gave 0.1672 gram of argentic chloride.

	Calculated for $C_6Cl_2(OHNH_2C_5H_{11})_2O_2$.	I.	II.
		Found.	
Chlorine	18.54	18.77	18.72

Properties of the Isoamylamine Chloranilate.—It is a purplish-red, crystalline substance ; slightly soluble in methyl or ethyl alcohol ; also somewhat soluble in glacial acetic acid, but decomposed by it ; essentially insoluble in benzol, ether, chloroform, acetone, ligroïn, carbonic disulphide, or ethyl acetate. Hydrochloric acid decomposes the salt, giving a solution of chloranilic acid, which was recognized by the purple color of its aqueous solution, and the formation from this solution of the characteristic red silver salt.

Action of Diisoamylamine on the Oxide,
$$C_6Cl_2OCH_3O(OCOC_4H_9)_2OCH_3.$$

After the study of the action of isoamylamine on the oxide, which has been just described, it seemed of interest to determine whether a secondary amine would act like a primary amine on the oxide, and accordingly we took up this work with diisoamylamine.

When to 1 gram of the oxide dissolved in hot benzol 2.5 grams of diisoamylamine were added, the solution turned yellow immediately, and this color finally gave place to red. On cooling, no solid separated, but after evaporating off part of the solvent a reddish compound appeared. To obtain this in quantity the greater part of the benzol was evaporated off on the steam-bath, and the rest was allowed to pass off spon-

taneously. The red solid left was washed thoroughly with water, and purified by crystallization, at first from a mixture of alcohol and water, and finally from ligroïn, until it showed the constant melting-point 168°–169°, when it was dried at 100°, and analyzed with the following result :

0.1245 gram of the substance gave, by the method of Carius, 0.0714 gram of argentic chloride.

	Calculated for $C_6Cl_2(C_6H_{11})_2N(OHNH(C_6H_{11})_2)O_2$.	Found.
Chlorine	14.06	14.17

Properties of the Diisoamylamine Salt of the Dichlordidiisoamyl-amidoxyquinone.—It separates from hot ligroïn in reddish-brown crystals, which melt at 168°–169°. It is very soluble in acetone, benzol, or chloroform ; soluble in cold alcohol, easily soluble in hot ; somewhat soluble in cold ligroïn, more freely in hot. The addition of an acid to the alcoholic solution sets free the oxyquinone, which usually is precipitated as an oil. Plumbic acetate, when added to the alcoholic solution, gave a greenish precipitate.

As the analysis and properties of this substance showed that diisoamylamine had acted on the oxide in precisely the same way as the isoamylamine, we decided not to pursue this line of work further.

Action of Diisoamylamine on Chloranil.

A small quantity of chloranil dissolved in hot benzol was treated with an excess of diisoamylamine. A green coloration was first noticed, which changed to brown in a short time, while a white crystalline substance was precipitated, which was recognized as the chloride of diisoamylamine by its properties. After the solution had been evaporated to a slight extent on the steam-bath, the insoluble diisoamylamine salt was filtered out, and the filtrate mixed with its own volume of alcohol allowed to evaporate spontaneously. After several hours, beautiful, purplish-black needles separated from the liquid, which were washed with alcohol, and finally recrystallized from alcohol. After drying *in vacuo* it gave the following result on analysis :

0.0971 gram of the substance gave, by the method of Carius, 0.0577 gram of argentic chloride.

	Calculated for $C_6Cl_2[(C_5H_{11})_2N]_2O_2$.	Found.
Chlorine	14.58	14.69

It is evident, therefore, that the diisoamylamine has acted on chloranil in the same way that isoamylamine acted.

Properties of Dichlordidiisoamylamidoquinone, $C_6Cl_2[(C_5H_{11})_2 N]_2O_2$.—It crystallizes from alcohol in long, reddish-black needles. The substance is far from stable, giving off an odor of diisoamylamine on standing in the air or in a desiccator. If exposed to the air for a long time, it turns first reddish-brown, and finally becomes an uninviting sticky mass. Owing to this slight stability we are unable to state its melting-point with certainty ; the highest melting-point observed for it was 77°–78°. It is very easily soluble in benzol, ether, ligroïn, carbonic disulphide, or chloroform ; soluble in alcohol or acetone ; insoluble in water. Alcohol is the best solvent for it. It dissolves in strong sulphuric acid, and this solution gives a precipitate, when diluted with water. Cold sodic hydrate has no apparent action on it.

Action of Phenylhydrazine on the Oxide, $C_6Cl_2OCH_3O(OCOC_2H_5)_2OCH_3$.

When the oxide is warmed gently with phenylhydrazine a yellow substance is formed, which recalls the yellow intermediate body formed by the action of isoamylamine on the oxide. Before we found that isoamylamine led to definite compounds with comparative ease, we devoted a great deal of time to the study of this phenylhydrazine product and its derivatives, but with no result of sufficient certainty to be described, for, although more stable than the yellow isoamylamine compound, this phenylhydrazine derivative is not stable enough to give good results on analysis. So far as our work has led to any formulas they are in harmony with what we should expect from our study of the behavior of isoamylamine.

Hydroxylamine apparently does not act on the oxide.

Dichlordimethoxyquinonedimethyldiacetylacetal,
$$C_6Cl_2(OCH_3)_2(OCOCH_3)_2(OCH_3)_2.$$

This substance and the ethyl compound described in the next section were prepared for the sake of comparison with the corresponding benzoyl acetals.

3.5 grams of the sodium salt of the dichlordimethoxyquinonedimethylhemiacetal were suspended in acetone, and 2 grams of acetyl chloride added with constant stirring. The action took place to some extent even in the cold, but to complete it the mixture was heated on the steam-bath for a short time, until most of the acetone had passed off. The product thus obtained was crystalline, and somewhat colored by chloranilic acid and dichlordimethoxyquinone. It was purified by washing with alcohol, water, and dilute sodic hydrate, to remove sodic chloride, chloranilic acid, and the red substituted quinone, and at last by crystallization from a mixture of chloroform and alcohol, until it showed the constant melting-point 177°–178°, when it was dried at 100°, and analyzed with the following result :

0.2031 gram of the substance gave, by the method of Carius, 0.1534 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OCOCH_3)_2(OCH_3)_2.$	Found.
Chlorine	18.44	18.67

Properties of Dichlordimethoxyquinonedimethyldiacetylacetal.— The substance crystallizes from a mixture of chloroform and alcohol in good-sized, white prisms, in which two basal planes are usually so well developed that the crystals look like thick plates. The edges also consist of two basal planes commonly, and the ends of two planes at an obtuse angle to each other. The form seems to be monoclinic. Another very common form consists of rhombic plates with bevelled edges and very sharp acute angles, which are frequently truncated by 2 planes, the enlargement of these planes forming the edges in the prisms described at first. It melts at 177°–178°.[1] It is easily soluble in chloroform ; soluble in benzol ; slightly soluble in ethyl or methyl alcohol, but more soluble in either of these solvents when hot ; slightly soluble in ether

[1] The corresponding benzoyl compound melts at 193°.

or acetone; almost insoluble in glacial acetic acid; essentially insoluble in ligroïn, carbonic disulphide, or water. A mixture of chloroform and alcohol is the best solvent for it. Sodic hydrate has no apparent action on it.

The most interesting work with this substance was to try to convert it into an oxide similar to the one obtained from the benzoyl acetal. For this purpose it was heated with sulphuric acid of specific gravity 1.44, but the only product which seemed to be formed in these experiments was chloranilic acid; no signs of an intermediate substance could be found. It appears, therefore, that the acetyl groups are far less firmly attached to the molecule in this class of compounds than the benzoyl groups.

Dichlordiethoxyquinonediethyldiacetylacetal,
$$C_6Cl_2(OC_2H_5)_2(OCOCH_3)_2(OC_2H_5)_2.$$

Six grams of the sodium salt of dichlordiethoxyquinone-diethylhemiacetal were suspended in a little acetone, and treated with 3 grams of acetyl chloride with constant stirring. The reaction took place even in the cold, but in order to be certain that it was complete the mixture was heated gently on the steam-bath for a few minutes. The product was washed with water, dilute sodic hydrate, and finally with a little alcohol, after which it was crystallized from a mixture of chloroform and alcohol, until it showed the constant melting-point 120°–121°, when it was dried, and analyzed with the following results:

I. 0.2059 gram of the substance gave, by the method of Carius, 0.1356 gram of argentic chloride.

II. 0.1740 gram of the substance gave 0.1126 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OCOCH_3)_2(OC_2H_5)_2$.	Found. I.	II.
Chlorine	16.09	16.28	16.00

Properties of Dichlordiethoxyquinonediacetyldiethylacetal.— This substance crystallizes from a mixture of chloroform and alcohol in very sharp rhombic plates with bevelled edges, and the acute angles often truncated. It resembles the methyl compound strongly in crystalline form and habit except that

the plates are usually thinner, and it crystallizes even more beautifully. It melts at 120°–121°,[1] and is soluble in benzol or chloroform; somewhat soluble in carbonic disulphide; slightly soluble in cold methyl or ethyl alcohol, more soluble in hot; insoluble in ligroïn or in water. A mixture of chloroform and alcohol is the best solvent for it. Sodic hydrate has no apparent action upon it.

Action of Sulphuric Acid on Certain Diatomic Phenols.

This work was undertaken in the hope that it might give some help in deciding whether the atom of oxygen in the oxide of dichlormethoxyquinonedibenzoylmethylacetal is in the ortho or meta position; for if by treating ortho or meta diatomic phenols with sulphuric acid we could obtain from the one or the other an oxide similar to that which we are studying, there would be a strong probability that the oxygen in our oxide was attached in the same position as that in the new oxide.

The phenols which we have used are resorcine as the meta body, pyrocatechine and some of its derivatives as the ortho compounds, and also chloranilic acid as a representative of the para series.

The sulphuric acid of specific gravity 1.44 used in making the oxide, $C_6Cl_2OCH_3O(OCOC_6H_5)_2OCH_3$, had no apparent effect on resorcine, but when it was boiled with an acid of specific gravity 1.71, a reddish-brown solution was formed, which deposited a brown mass on cooling; this dissolved in sodic hydrate, and was reprecipitated by hydrochloric acid. From its properties there can be little doubt that it is the resorcine ether, $(C_6H_4OH)_2O$, and therefore that 2 molecules of resorcine have taken part in its formation.

Sulphuric acid of specific gravity 1.44 had no apparent effect on chloranilic acid.

Sulphuric acid of 1.44 specific gravity did not act on pyrocatechine, and when an acid of 1.84 specific gravity was used the substance was charred. When guaiacol was boiled with sulphuric acid of specific gravity 1.44 for three to four hours, the liquid turned purplish-black, and on standing a small quantity of a

[1] The corresponding benzoyl compound melts at 170°.

black amorphous substance separated, which we have not yet succeeded in obtaining in sufficient quantity for identification; but, as it became colorless when treated with zinc and sulphuric acid, and this reduction-product was turned yellow by dilute nitric acid, it seems certain that it is not the desired oxide. It probably belongs to the class of quinones. We hope that the study of this body will be continued in this laboratory in the coming year. In the hope that the loading of the benzol ring with bromine atoms would make the substance more stable, and at the same time encourage the formation of an oxide, since our oxide was prepared from a body with negative radicals on the ring, we next tried the action of sulphuric acid on tetrabromveratrol. With weaker acids no change was observed, but, when it was heated with an acid of specific gravity 1.84, a dark-colored solution was formed, and sulphurous dioxide was given off; after dilution with water a red substance was precipitated, which we inferred was tetrabromorthoquinone from its color, and the fact that the sulphuric acid had given up oxygen in forming it. We have not succeeded as yet in obtaining anything resembling our oxide from any of the other brompyrocatechines or their ethers which we have tried.

Tetrabromguaiacol, $C_6Br_4OCH_3OH$.

This substance was made in connection with the work just described, as follows: Five cc. of bromine (a considerable excess over the 4 molecules required) were added slowly to 2 grams of guaiacol. The reaction was very violent, hydrobromic acid being given off copiously, and before all the bromine had been added the oil solidified to a white mass. After the reaction had been rendered complete by heating for a short time on the steam-bath, the product was crystallized from hot chloroform, until it showed the constant melting-point 162°–163°. The same substance was obtained by adding the guaiacol to the bromine. It was dried at 100°, and analyzed with the following result:

0.2635 gram of the substance gave, by the method of Carius, 0.4485 gram of argentic bromide.

	Calculated for $C_6Br_4OCH_3OH.$	Found.
Bromine	72.71	72.44

Properties of Tetrabromguaiacol.—It crystallizes from chloroform in long, white, slender prisms, or thick needles with square ends; and melts at 162°–163°. It is easily soluble in acetone or ether; soluble in ethyl or methyl alcohol, or in chloroform, much more soluble in hot than in cold chloroform; somewhat soluble in benzol, or carbonic disulphide; slightly soluble in glacial acetic acid, or ligroïn; insoluble in water. It dissolves easily in an alcoholic solution of sodic hydrate; and in an aqueous solution of sodic hydrate, if it is hot. Acids precipitate the unaltered substance from either of these solutions. When a solution of tetrabromguaiacol in warm glacial acetic acid is treated with strong nitric acid, a red body is formed which we think is tetrabromorthoquinone.

Tribromveratrol, $C_6HBr_3(OCH_3)_2.$

This substance was prepared from tribromguaiacol made by the action of bromine on an alcoholic solution of guaiacol according to Tiemann and Koppe.[1] 4 grams of the tribromguaiacol were heated in a flask with a return-condenser with 0.45 gram of sodic hydrate dissolved in about 50 cc. of methyl alcohol and an excess of methyl iodide. After heating for about an hour the solution was concentrated somewhat on the steam-bath, when upon cooling a large quantity of white crystals separated. These were washed with dilute sodic hydrate to remove any unaltered tribromguaiacol, and then with water; after which they were recrystallized from alcohol until they showed the constant melting-point 86°–87°, when the substance was dried *in vacuo*, and analyzed with the following results:

I. 0.2094 gram of the substance gave, by the method of Carius, 0.3108 gram of argentic bromide.

II. 0.1196 gram of the substance gave 0.1795 gram of argentic bromide.

[1] Ber. d. chem. Ges., **14**, 2017.

	Calculated for $C_8HBr_3(OCH_3)_2$.	I.	Found. II.
Bromine	64.00	63.19	63.87

Properties of Tribromveratrol.—It crystallizes from hot alcohol in long, slender, slightly branched, white needles, which when well developed have blunt, perhaps square, ends. It melts at 86°–87°. It is easily soluble in benzol, chloroform, acetone, or ethyl acetate ; soluble in ligroïn ; somewhat soluble in methyl or ethyl alcohol, or in glacial acetic acid, much more soluble in each of these solvents when hot. The best solvent for it is hot alcohol. Sodic hydrate does not dissolve it, and does not decompose it even when boiling. A warm, glacial acetic acid solution of tribromveratrol turns bright-red, when strong nitric acid is added to it. If tribromguaiacol is treated in the same way, a similar red color is produced, and a bright-red substance is deposited on cooling, which we supposed was tribromorthoquinone, but owing to the small yield and the late date at which this work was undertaken we are unable to make any definite statement in regard to it. We hope that the study of this substance will be continued in this laboratory during the coming year.

Colored Compounds Obtained from Substituted Quinones by the Action of Sodic Alcoholates.

The work described in this section was undertaken in the hope of preparing new hemiacetals derived from the substituted quinones, and also of throwing more light on the nature of quinhydrone and phenoquinone. It was abandoned before it had reached a satisfactory conclusion, because of the appearance of two papers by Astre,[1] in which he described substances similar to those made by us ; but we give an account of it here, as it has led us to differ from Astre in regard to the constitution of these bodies.

In the paper[2] on hemiacetals derived from quinones, Grindley and one of us state that the first product of the action of sodic phenylate on chloranil is a green or black substance, which on heating passes rapidly into the red dichlordiphenoxyquinone. As it seemed possible that this might be a diphenyl-

[1] Compt. rend., **121**, 326, 530.   [2] This JOURNAL, **17**, 595.

hemiacetal, we spent some time in trying to isolate it ; but, although we succeeded in obtaining a dark-green substance in the solid state, we were unable to find any method of freeing it from the sodic chloride, which (in addition to dichlordiphenoxyquinone) was always formed by a secondary reaction, since it was very unstable. We next turned our attention to the green compound formed by the action of sodic methylate on chloranil,[1] as this from its mode of formation and color seemed to be analogous to the phenoxy compound. Here we were more successful. A sample of this green product of the action of sodic methylate on chloranil was washed with equal parts of methyl alcohol and water, which did not decompose it so rapidly as water alone, then with methyl alcohol alone, and finally with benzol. It gave the following result on analysis, after it had been dried *in vacuo* :

0.1810 gram of the substance gave 0.0418 gram of sodic sulphate.

	Calculated for $C_6Cl_4O_2CH_3ONa$.	Found.
Sodium	7.66	7.48

Our other analyses pointed to a similar composition for this substance and related compounds, but in no other case were we so fortunate as to obtain a sample free from sodic chloride. We should not venture to publish this single analysis, therefore, if it were not confirmed by the results given by Astre, who made a green compound by the action of potassic ethylate in ethereal solution upon quinone, which had the formula $C_6H_4O_2KOC_2H_5$, and a similar substance with alcoholic potassic hydrate, $C_6H_4O_2KOH$. Our attempts to prepare compounds like these for analysis have given us a high appreciation of the experimental skill which Astre has shown in purifying these substances. That his compounds are analogous to ours we think can admit of no doubt ; not only on account of the analyses, but from the method of formation and the color.

Astre, however, does not assign to his compounds the formulas given above, but considers that the potassium has replaced one of the atoms of hydrogen attached to the benzol

ring, so that the substances contain alcohol or water of crystallization, thus: $C_6H_3KO_2C_4H_5OH$ and $C_6H_3KO_2H_2O$. His principal reason for this is based on his experiment with metallic potassium and an ethereal solution of quinone. In this case he found that hydrogen was given off, and a green compound formed having the formula $(C_6H_3KOOH)_2C_4H_{10}O$, which amounts to a molecule of dipotassic quinhydrone combined with one molecule of ether. The attempt to apply Astre's theory to our compound leads to the inadmissible formula $C_6Cl_3NaO_2CH_3OCl$, and therefore, if his compounds and ours are similarly constituted, his theory must be abandoned. In this case it is necessary to explain his result with metallic potassium and quinone in ethereal solution, and this can be done perhaps by supposing a very minute quantity of water or alcohol to have been present in the ether used. This would have given nascent hydrogen, which would have formed a little quinhydrone; this quinhydrone then, by acting on the potassium, would give its salt and more nascent hydrogen, which would continue the action, until a considerable amount of the potassium salt of the quinhydrone had been formed. As quinhydrone forms salts with the metal probably attached to oxygen,[1] it is not necessary to assume that the atom of potassium has replaced the hydrogen on the benzol ring in this case. All these compounds, by their mode of formation, marked colors, and slight stability, recall the substances formed by the action of sodic alcoholates on various nitro compounds, (such as trinitrobenzol,[2] symmetrical dinitrobenzoic acid,[3] bromdinitrobenzoic acid, and bromdinitrotoluol,[4]) and we think probably belong to the same class. The lamented Victor Meyer had already proposed a theory to account for these substances similar to that of Astre, since he assumed that an atom of hydrogen on the benzol ring was replaced by sodium in these bodies, but it is hard to bring this theory into accord with some of the facts published since it was proposed, and the whole subject needs further investigation.

[1] Jackson and Oenslager: This JOURNAL, **18**, 15.
[2] Lobry de Bruyn: Rec. Trav. Chim. Pays-Bas., **14**, 89.
[3] Victor Meyer: Ber. d. chem. Ges., **27**, 3153.
[4] Jackson and Ittner: This JOURNAL, **19**, 199.

We shall not describe our numerous experiments in regard to these colored derivatives of the quinones, but content ourselves with simply mentioning the substances observed by us. Chloranil gave in addition to the green compounds with sodic methylate and phenylate already mentioned a similar product with sodic amylate. Trichlorquinone also gave a green product with sodic methylate or amylate. Trichlorquinone, or chloranil, gave a blue compound with a strong solution of sodic hydrate, and we also observed the formation of a blue product from sodic hydrate and quinone before the appearance of Astre's paper. With sodic methylate, or amylate, quinone gave blue substances, undoubtedly similar to the ethylate product analyzed by Astre. Hydroquinone gave a faint bluish-green coloration with sodic hydrate in aqueous solution, and a bluish-green color when sodic methylate was added to its solution in benzol.

Action of Iodine and Sodic Hydrate on Chloranilic Acid.

We had hoped to extend our work to the reduction-product obtained from the ethyl oxide by Grindley and one of us,[1] and accordingly tried to reduce the oxide,

$$C_6Cl_2OCH_3O(OCOC_6H_5)OCH_3,$$

with hydriodic acid in the way used for the ethyl oxide, but we found that, whereas the ethyl compound was easily reduced, as described in the place cited, the methyl oxide was not at all affected under the same conditions, and no satisfactory result was obtained, even when much higher temperatures were used. To the product of one of these experiments, which contained unaltered oxide and free iodine, sodic hydrate was added, when a yellow body separated, which had the smell of iodoform. This observation led us to try the action of iodine on an alkaline solution of sodic chloranilate, when we found that even at as low temperatures as 50°–60° iodoform was obtained. This was recognized by its melting-point, 119°, its odor, its yellow color, and the fact that it crystallized in the hexagonal system, although it appeared in stars like snowflakes instead of the usual hexagonal plates.

[1] This JOURNAL, **17,** 641.

The work with the reduction-product was begun so late in the year that no definite results were obtained before the close of the laboratory for the vacation.

REVIEWS.

Nozioni di Analisi Chimica e Cenni sull' Analisi delle Acque Potabili, del Dott. Icilio Guareschi, professore ordinario di Chimica Farmaceutica e Tossicologica nella R. Università di Torino. Unione Tipografico-editrice. Torino. 1898.

This little book, of 172 pages, is intended to provide an elementary manual of qualitative chemical analysis in general, mainly of inorganic substances, with special chapters on "microchemical" work and on the examination of potable waters. Hence the greater part is necessarily a reproduction, with but little novelty of form, of what has appeared in numberless other manuals in various languages.

A few points give a certain degree of originality to the mode of treatment of the well-worn subject. Thus, in the preliminary chapter devoted to "nozioni generali," the nature of the reactions made use of for analytical purposes is stated with rather more fulness than in many books, including reference to such matters as the modern ideas of dissociation of *ions* in solution, chemical stability and activity under varying physical conditions, etc. Among the directions for the identification of individual basic and acid radicles a few reactions are mentioned which are not in general use, as, for instance, the detection of mercury in mercuric salts by the formation of the blue crystalline double thiocyanate of mercury and cobalt, and a few substances are to be found here which are not very commonly included in the list of those to be detected, such as trichloracetic and lactic acids.

In the chapter on microchemical analysis there are some useful suggestions as to the production of crystalline precipitates easily recognizable by their microscopic appearance, including some rather unusual substances, such as the antimonio-tartrate of barium, and the double acetate of uranyl and sodium. Throughout the work there are numerous and, in general, good figures of specimens as seen under the microscope. The only part in which quantitative methods are discussed is that on the examination of natural waters for domestic use.

Although the name of Professor Guareschi, of the University of Turin, appears on the title-page, the book seems to have been prepared by other hands from notes of his lectures and laboratory teachings.   J. W. M.

the oft-encountered one-sidedness which can see, as in the fable of the gold and silver-faced shield, only matter or only energy, though we have ever before us in nature the mysterious association of the two. Yet, as has been said, this critical article is worth reading—not so much for the depreciatory criticism as for the glimpse it gives of the perpetual struggle onwards *towards* truth, with so much toil and so much partially ineffective labor on the part of even the strongest in the army of science.   J. W. M.

SPECTRUM ANALYSIS. By JOHN LANDAUER, LL.D. Authorized English edition by J. BISHOP TINGLE. New York : John Wiley & Sons.

As stated in the author's preface, "this work originated as a reprint of an article on Spectrum Analysis recently contributed to Fehling-Hell's 'Neues Handwörterbuch der Chemie.'"

Its object, as explained in the translator's preface, is to fill a gap which has long been felt in the teaching of spectrum analysis as a branch of chemistry. The translator says, " the claim of spectrum analysis to a place in a chemical curriculum is steadily obtaining increased recognition, and its importance is generally admitted both for students preparing for teaching and for those who wish to engage in technological work." He adds that "there has been no attempt to treat the subject exhaustively, but rather to indicate the more salient points of theory, etc., leaving it to the teacher to complete and extend them at his own discretion." The plan of the book may be judged from the contents, which are divided into ten chapters.

Chapter I is introductory and historical.

Chapter II deals with the physical properties of light, such as refraction, dispersion, and diffraction.

Chapter III describes various forms of prismatic and grating spectroscopes.

Chapter IV contains descriptions of spectroscopic instruments and Rowland's concave grating apparatus.

Chapter V contains descriptions of various spectroscopic adjuncts such as are necessary for the investigation of flame-, arc-, spark-, and absorption-spectra.

Chapter VI discusses emission spectra from the physical standpoint, giving an account of Kirchhoff's law and all the laws concerning absorption, fluorescence, etc. In this same chapter also are discussed the various relations which exist between the lines of the spectrum of any one element or between the spectra of different elements.

In chapter VII there are given tables of wave-lengths of all the elements, together with those of many of the compounds.

Chapter VIII deals with absorption-spectra, giving the results of the best investigations.

Chapter IX discusses the solar spectrum, including the results of observations of different portions of the sun and the theories which have resulted from these observations.

Chapter X describes the spectrum of other celestial bodies, such as planets and the fixed stars. There is also a brief account of auroras, of lightning, and the question as to the displacement of lines owing to motion in the line of sight.

It is evident that the scope of the work is very wide, and it may be said in the main that the purposes of the book are well carried out. The translation is excellent and the arrangement of the matter is all that can be desired. The index and the references in the different chapters are most satisfactory. It is a pleasure to have a book so well fitted for actual use as the one before us. The book is in every way well suited for the object for which it is written, namely to serve as a guide for practical laboratory work for students of chemistry ; and it is to be recommended most heartily.

There are, however, various points which it is the duty of the reviewer to mention—errors of omission, as well as errors of commission. Some of these could be easily corrected in later editions which it is to be hoped will be called for before many months. The system of abbreviations used throughout the book is most unsatisfactory. The scientific world has become so thoroughly accustomed to the abbreviation "Phil. Mag." for the "Philosophical Magazine," and "Pogg. Ann." for Poggendorf's Annalen," that it is not at all desirable at the present time to change these well-known symbols for such unsuggestive ones as " P. M." and " P. A." An abbreviation ought to have the merit of suggesting something in itself, and such as these, " P. T." and " P. R. S.," etc., are not to be recommended.

Again, in mentioning Scheiner's most excellent treatise on Spectrum Analysis of the Stars, it should be added that there is an English translation by Frost, which in some respects is superior to the German original. There seems to be no reason also, if Higgs's photographic atlas of the normal solar spectrum is mentioned, why Rowland's standard map of the same spectrum should not also be included.

There are various matters of importance which are not mentioned in the book, some of which certainly deserve notice. Among these may be mentioned the use of the radio-micrometer as an instrument of research in the ultra-red spectra ; the results of the work by Humphreys and Mohler on the effect of the pressure on the arc, results which are some of

the most important obtained in recent years ; the law recently
discovered by Rydberg and Schuster on the relations between
the different series in the spectrum of any one element ;
Michelson's work on the constitution of various spectrum
lines and his determination of the value of the standard metre
in terms of wave-lengths. There are many other matters
which one might expect to see discussed, but it may be that
the work went to press before the results were well known.
These, however, which are mentioned above, certainly ought
to appear. It must be said too that from a physical standpoint
many of the sections in the book are unsatisfactory. The
chapter devoted to prisms and gratings is not at all what
might be desired, and in regard to gratings particularly there
are several statements which are not correct. It would have
been easy to have given an elementary theory of the plane
grating, which would have been useful to all students, what-
ever their acquaintance with physics. The description of the
Zeeman effect on page 75 is also incomplete. The section on
the absorption of solutions on page 79 is not as full nor as
definite as it should be. Within recent years the study of
the absorption of solutions has obtained such prominence and
measurements are now made so accurately that this subject
would seem to demand more careful treatment than it receives
here. In several places in the book, too, the spark spectrum
is spoken of as having a higher temperature than the arc ; a
statement which is misleading, because it can hardly be said
that a spark has a temperature.

In conclusion, it may be said that the book before us is the
most satisfactory of any that is at present available for stu-
dents. The paper, type, and the illustrations are excellent ;
and special praise should be again given the references and
the index. The book may be placed safely in the hands of
all students, and is to be recommended to both teacher and
class.   J. S. A.

Der Praxis der Molekelgewichtsbestimmung. Von Heinrich
  Biltz, Privatdocent an der Universität in Greifswald. Fischer's
  Medicinische Buchhandlung. H. Kornfeld, Berlin. 1898. pp. 170.

The determination of the molecular weights of substances
has become a familar laboratory operation. The methods
which apply to the vapors of substances enable us to decide
the question, how many molecules are aggregated into a unit
when the compound in question is present as a gas, while the
freezing-point and boiling-point methods furnish us with the
means of ascertaining the molecular weights of substances in
solution in a given solvent.

The purpose of the work in hand is to describe and discuss

these methods for the purpose of application in the chemical laboratory. And since complicated cases often arise during the progress of chemical investigations, a comparatively thorough and elaborate treatment of the available methods is deemed necessary by the author.

The determination of the molecular weights of substances in the form of vapor is taken up first, and the methods of Dumas, Gay Lussac, Hofmann, and V. Meyer, are treated of at some length. This is followed by a discussion of the freezing-point and boiling-point methods for determining the molecular weights of substances in solution. The apparatus of Beckmann for carrying out these methods is described, together with various improvements which have been made by different experimenters, for the purpose of increased accuracy.

The book concludes with a description of the method of Traube, for determining the molecular weights of pure substances in the liquid or solid form, from their molecular volumes. But the author states in his preface that "the results must be used with considerable care until the method has been more completely investigated and applied."

One notices the absence of the beautiful method of Ramsay and Shields for determining the molecular weights of liquid substances from their surface-tension. This was probably omitted, because the measurement of surface-tension is not altogether simple, and it can hardly be hoped that this method will ever be generally used in the laboratory.

The book is clear, concise, and in every particular an admirable piece of work. It seems that an English translation would be useful.   H. C. J.

DAS OPTISCHE DREHUNGSVERMÖGEN ORGANISCHER SUBSTANZEN UND DESSEN PRAKTISCHE ANWENDUNGEN. Bearbeitet von DR. H. LANDOLT, Professor der Chemie an der Universität zu Berlin. Unter Mitwirkung von DR. O. SCHÖNROCK, DR. P. LINDNER, DR. F. SCHÜTT, DR. L. BERNDT, DR. T. POSNER. Zweite gänzlich umgearbeitete Auflage, mit eingedruckten Abbildungen. Druck und Verlag von Friedrich Vieweg und Sohn. 1898. pp. 655.

The first edition of this book appeared eighteen years ago, when the subject was comparatively undeveloped. The number of active substances known, has not only increased from 300 to more than 700, but optical activity has acquired far deeper significance since van't Hoff and Le Bel pointed out the relation between rotation and constitution.

In this comprehensive work the author distinguishes between three classes of optically active substances. Those which rotate the plane of polarization only when crystalline, those which rotate when either crystalline or amorphous, and

those which are active when amorphous, in the liquid state and in solution. After considering the theory of the asymmetric carbon atom, the methods for obtaining active from inactive substances, involving crystallization, the use of alkaloid salts, and the use of bacteria, are taken up.

The second part of the book deals with the relation between the amount of rotation, and the physical conditions employed, such as wave-length of light, temperature, etc.

The third part of the book is of most direct interest to the physical chemist, since it discusses the problem of the rotation of substances in solution, and thus bears directly upon the theory of electrolytic dissociation.

The fourth part, written by Schönrock, describes exhaustively the forms of apparatus employed in measuring the amount of rotation—the polarizer, saccharimeter, lamps, tubes for holding the liquids, etc.

Schütt has written part 5, on the practical applications of optical rotation—such as the determination of the amount of sugar, glucose, camphor, nicotine, etc.

The sixth, and last, division comprises the data which were obtained up to 1896.

The accuracy and thoroughness of this book are both insured by the name of its author.   H. C. J.

AMERICAN

CHEMICAL JOURNAL

THE ACTION OF ZINC ON COPPER SILICIDE.

By G. de Chalmot.

It was shown in previous articles that copper and silicon have only a feeble affinity for each other. The compound Cu_2Si is readily decomposed by many agents.

I have also communicated the fact that copper silicide can be decomposed by sulphur in such a manner that the silicon is obtained in free condition. I have looked for other reagents which will liberate the silicon from the copper without combining with it. It is not easy to find such reagents, for silicon, especially in *status nascendi*, is one of the most active substances. It is known, however, from the work of Vigoureux[1] that certain metals like zinc, tin, and aluminium do not unite with silicon. These metals readily form alloys with copper, and there was a possibility that their affinity for copper is greater than that of silicon.

I have actually found that zinc decomposes copper silicide, liberating the silicon. The reaction is a partial one. The more zinc there is present the more silicon there is separated from the copper.

This reaction is remarkable in so far as it shows that the affinity between the two metals, zinc and copper, is as great or greater than that between copper and silicon. Copper sili-

[1] Compt. rend., **123**, *115*.

cide is undoubtedly a chemical compound, for the silicon in it is much more active than free silicon, being very readily oxidized. The copper in it does not dissolve in mercury and dissolves more easily in dilute acids than free copper. Vigoureux, moreover, obtained copper silicide in crystalline, pure condition. We may then take the reaction of the zinc with this copper silicide as additional evidence of purely chemical character in favor of the view that brass contains distinct chemical compounds.

The study of this reaction also seems to indicate that among the compounds, which copper and zinc form with each other, that compound which contains most copper has a composition not differing very far from the formula $ZnCu_2$. This result agrees with that of Charpy.[1] Neither tin nor antimony attacks copper silicide, which shows that they have less affinity for copper than zinc.

In carrying out the experiments the copper silicide was melted in a crucible, and the molten zinc was added. The mass was stirred and allowed to cool. A part of the zinc always burned up and often some silicon, as will appear from the following figures.

The silicon that is liberated is always crystalline. Probably it dissolves in the zinc or in the brass compounds and crystallizes on cooling. A silicide of the following composition was used :

<center>*Silicide No. 1.*</center>

		Per cent.
Cu		90.53
Fe		0.21
Si		9.26
Free Si		trace

or,

	Per cent.
Copper silicide : Cu_2Si	50.08
Free copper	49.62
Iron silicide	0.30

This silicide contains only traces of free silicon and very little iron, which facilitates the comparison of the results.

This silicide was mixed with increasing quantities of zinc

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[1] Compt. rend., **122**, 670.

amounting to $\frac{1}{4}$, $\frac{1}{2}$, 1, $1\frac{1}{2}$, $1\frac{3}{4}$, and 2 times the weight of the silicide.

The zinc which was used was 99.69 per cent. pure. It contained as impurities, besides some carbon, mainly iron. It was free of all metals that in acid solutions are precipitated by hydrogen sulphide. I assumed that the iron in the original silicide was united with one-half its weight of silicon. I further assumed that all the mixtures contained about 0.25 per cent. iron, which is derived partly from the silicide and partly from the zinc. It is improbable that the iron from the zinc should unite with the liberated silicon at the low temperatures which were used, hence I calculated it as being in the free condition. I made these assumptions to save many analyses and to help in the calculations. The quantities of iron are really so small that they cannot materially affect the result.

In the mixtures, copper, total silicon, and free silicon were determined. The amount of iron derived from the silicide was found by assuming that it varies in the same ratio as the copper. By subtracting this amount of iron from the assumed total amount of iron, 0.25 per cent., I found the amount of free iron derived from the zinc. The remainder of the sample, after deducting copper, silicon, and iron, was taken to be zinc. The following are the results obtained :

Experiment I.

1 part silicide, $\frac{1}{4}$ part zinc.

	Per cent.
Cu	72.56
Fe	0.25
Zn	20.04
Si	7.15
Free Si	trace

or,

	Per cent.
Copper silicide : Cu_2Si	38.66
Other copper	40.97
Iron silicide	0.24
Free iron	0.09
Zinc	20.04

Experiment II.

1 part silicide, $\frac{1}{2}$ part zinc.

	Per cent.
Cu	61.92
Fe	0.25
Zn	31.73
Si	6.10
Free Si	0.99

or,

	Per cent.
Copper silicide : Cu_2Si	27.56
Other copper	39.40
Iron silicide	0.21
Free iron	0.11
Zinc	31.73
Free silicon	0.99

Experiment III.

1 part silicide, 1 part zinc.

	Per cent.
Cu	46.94
Fe	0.25
Zn	48.29
Si	4.52
Free Si	2.02

or,

	Per cent.
Copper silicide : Cu_2Si	13.40
Other copper	35.99
Iron silicide	0.15
Free iron	0.15
Zinc	48.29
Free silicon	2.02

Experiment IV.

1 part silicide, $1\frac{1}{2}$ part zinc.

	Per cent.
Cu	38.90
Fe	0.25
Zn	57.52
Si	3.33
Free Si	2.88

or,

	Per cent.
Copper silicide : Cu_2Si	2.25
Other copper	37.06
Iron silicide	0.13
Free iron	0.16
Zinc	57.52
Free silicon	2.88

Experiment V.

1 part silicide, $1\frac{3}{4}$ part tin.

	Per cent.
Cu	35.34
Fe	0.25
Zn	61.23
Si	3.18
Free Si	2.87

or,

	Per cent.
Copper silicide : Cu_2Si	1.48
Other copper	34.13
Iron silicide	0.12
Free iron	0.17
Zinc	61.23
Free silicon	2.87

Experiment VI.

1 part silicide, 2 parts zinc.

	Per cent.
Cu	32.83
Fe	0.25
Zn	63.95
Si	2.97
Free Si	2.79

or,

	Per cent.
Copper silicide : Cu_2Si	0.82
Other copper	32.16
Iron silicide	0.11
Free iron	0.17
Zinc	63.97
Free silicon	2.79

When the percentage of zinc increases the percentage of copper silicide decreases of course. But it can also be seen

from these figures that the copper silicide decreases much more rapidly than the copper. This is due to the more thorough decomposition of the copper silicide as the amount of zinc increases. This is especially evident in the following table :

	Ratio of copper to zinc.	Per cent. of the silicon in a free condition.[1]
Original silicide	100 : 0	trace
Experiment I	100 : 27.6	trace
" II	100 : 51.2	16.4
" III	100 : 102.9	45.2
" IV	100 : 147.8	87.5
" V	100 : 173.3	91.4
" VI	100 : 194.8	94.9

When the ratio of copper to zinc is 100 : 195, 94.9 per cent. of the silicon is in the free condition. The quantity of silicon then becomes so small that the difference between the amount of total and of free silicon comes within the limits of analytical errors.

Another obvious point is, that the addition of $\frac{1}{4}$ part of zinc does not liberate any silicon, while the addition of $\frac{1}{2}$ part liberates a considerable amount. I have repeated experiments I. and II., with the same result, so that there can be no doubt as regards this point. It can readily be explained by assuming that in experiment I. the zinc found sufficient free copper to satisfy its affinity and that in experiment II. it did not. The zinc then left the copper silicide alone in experiment I., but in II. a contest has started between the zinc and silicon for the possession of the copper. If this be true, we can conclude that the composition of that compound of copper and zinc, which contains the highest amount of copper, is within the limits of

20.04 parts Zn : 40.97 parts Cu = 32.8 per cent. Zn and 67.2 per cent. Cu,

and

31.73 parts Zn : 39.40 parts Cu = 44.6 per cent. Zn and 55.4 per cent. Cu.

[1] I have in each case deducted from the total amount of silicon that which is united to iron and I give the free silicon in per cents. of this deducted amount.

Judging from the large amount of free silicon in experiment II. we should expect the composition of this compound to be rather near the highest limit for copper. Such a compound might have the composition $ZnCu_2$, which contains 32.6 per cent. copper and 67.4 per cent. zinc. Charpy concluded from his experiments on the compounds in brass that the compound containing most copper has the composition $ZnCu_2$.

If we use a copper silicide containing less free copper we should expect that more silicon is liberated by the same amount of zinc, because the zinc and the silicon will sooner meet each other in a contest for the copper. The results have confirmed this belief.

I used a silicide which contains :

Silicide No. 2.

	Per cent.
Cu	81.14
Fe	2.52
Si	16.34
Free Si	4.37

or,

	Per cent.
Copper silicide : Cu_2Si	51.8
Free copper	38.8
Iron silicide	5.0
Free silicon	4.4

There is 4.37 per cent. free silicon in the sample, and I have therefore assumed the iron to be saturated with silicon. Supposing the iron to have been only half saturated with silicon, the results are still striking, as the figures given further below show.

To silicide No. 2 was added $\frac{1}{2}$ part of zinc. The product contains :

Experiment VII.

I part silicide, $\frac{1}{2}$ part Zn.

	Per cent.
Cu	54.51
Fe	1.68
Zn	32.71
Si	11.10
Free Si	6.77

or,

	Per cent.
Copper silicide : Cu_2Si	14.2
Other copper	42.9
Iron silicide	3.4
Zinc	32.7
Free silicon	6.8

From these results the following table is prepared. If we compare it with experiments II. and III., we see that the same amount of zinc has liberated more silicon from silicide No. 2 than from silicide No. 1 :

	Ratio of copper to zinc.	Per cent. of silicon in free condition.	
		Supposing all iron is saturated with silicon.	Supposing the iron is half saturated with silicon.
Silicide No. 2	100 : 0	31.6	29.0
Experiment VII	100 : 60	71.9	66.0
Silicon liberated by zinc		40.3	37.0

The amount of silicon which has been liberated by 60 parts of zinc is here 37–40.3 per cent., while 51.2 parts of zinc in experiment II. liberate only 16.4 per cent. of silicon from silicide No. 1, and 102.9 parts of zinc in experiment III. liberate 45.2 per cent., which is just a little more than 60 parts liberate from silicide No. 2.

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CVII.—ON THE COLORED COMPOUNDS OBTAINED FROM SODIC ALCOHOLATES AND PICRYL CHLORIDE.[1]

BY C. LORING JACKSON AND W. F. BOOS.

The work described in this paper is the continuation of a research begun by M. H. Ittner and one of us,[2] about three years ago, upon the colored products of the action of sodic alcoholates on certain aromatic nitro compounds. For a statement of the work of Lobry de Bruyn and Van Leent, and of Victor Meyer, on this subject, the reader is referred to that paper. The first object to which we turned our attention

[1] Presented to the American Academy of Arts and Sciences, January 12, 1898.
[2] This JOURNAL, **19**, 199.

was the isolation and analysis of more substances of this class, since only three analyses of these bodies have been published. These three analyses led to the following formulas :

$$C_6H_2(NO_2)_3KOCH_3\tfrac{1}{2}H_2O ;[1]$$
$$[C_6H_2(NO_2)_3COOKKOCH_3]_2CH_3OH ;[2]$$
$$\text{and } C_6H_2OCH_3(NO_2)_2COONaNaOC_2H_5.[3]$$
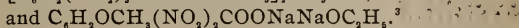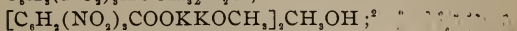
As dinitranisic acid had given Ittner and one of us a comparatively stable compound, when treated with sodic ethylate, we at first tried to prepare similar compounds from it and other sodic alkylates; but a few experiments convinced us that the products from these reactions were too unstable for our purpose. Our attention was then called by one of our associates in this laboratory to the red substance formed by the action of sodic methylate on picryl chloride, and this has led to the discovery and analysis of the following compounds :

$$C_6H_2(NO_2)_3OCH_3NaOCH_3,$$
$$C_6H_2(NO_2)_3OC_2H_5NaOC_2H_5,$$
$$C_6H_2(NO_2)_3OC_3H_7NaOC_3H_7,$$
$$C_6H_2(NO_2)_3OC_6H_{11}NaOC_6H_{11},$$
$$C_6H_2(NO_2)_3OCH_2C_6H_5NaOCH_2C_6H_5;$$
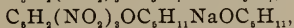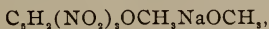
to which should be added a substance formed by the action of aqueous baric hydrate on a solution of trinitranisol in methyl alcohol, probably

$$[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2,$$

which was also obtained crystallized with 10 molecules of water. All of these substances have vivid red colors, and are decomposed by an acid, or more slowly by water, giving the picric ether. They are remarkably stable for compounds of this class.

The study of these substances has thrown some light on their constitution. The only published theory about bodies of this class is the suggestion made by the lamented Victor Meyer in his first paper[4] on this subject, that they might be formed by the replacement of one of the atoms of hydrogen on the benzol ring by potassium or sodium. According to

[1] Lobry de Bruyn and Van Leent: Rec. Trav. Chim. Pays-Bas., **14**, 150.
[2] Van Leent: *Ibid*, **15**, 89.
[3] Jackson and Ittner: This JOURNAL, **19**, 210.
[4] Ber. d. chem. Ges., **27**, 3153.

this view our methyl compound would be formulated as follows: $C_6HNa(NO_2)_3OCH_3CH_3OH$; that is, it would contain a molecule of methyl alcohol of crystallization. Lobry de Bruyn[1] has brought forward an almost, if not absolutely, conclusive argument against this theory in his observation that sodium does not act on trinitrobenzol, even when in a boiling xylol solution, and therefore that trinitrobenzol cannot contain an atom of hydrogen which can be replaced by sodium. Our work described in this paper furnishes two arguments which confirm that of Lobry de Bruyn. First, it has shown that all of the substances analyzed so far contain, according to this theory, one molecule of alcohol of crystallization, while the salt without alcohol of crystallization predicted by it ($C_6HNa(NO_2)_3OCH_3$, for instance) has never been obtained. Second, we have found that the methyl compound $C_6H_2(NO_2)_3OCH_3NaOCH_3$ can be heated to 130° without loss of weight, which could not have been the case had it contained methyl alcohol of crystallization, as is required by this theory. While neither of these arguments is so convincing as that derived by Lobry de Bruyn from the action of metallic sodium, they give it strong confirmation,[2] and we are satisfied therefore that Victor Meyer's theory in regard to these bodies should be abandoned, and that they should be considered as formed by the addition of the sodic alcoholate to the aromatic nitro compound. Whether the alcoholate is added to the carbon of the benzol ring or to the nitro group cannot be determined with our present knowledge, but possibly a way has been opened to decide this question by the discovery of the addition compounds formed from quinone and potassic ethylate or hydrate described by Astre,[3] $C_6H_4O_2KOC_2H_5$ and $C_6H_4O_2KOH$, and that from chloranil and sodic methylate, $C_6Cl_4O_2NaOCH_3$, obtained by H. A. Torrey and one of us.[4] These substances, by their striking colors, their formulas, mode of formation, and slight stability, seem to be related

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[1] Rec. Trav. Chim. Pays-Bas., **14**, 89.

[2] Ittner and one of us (This JOURNAL, **19**, 212) observed that the compound $C_6H_2(NO_2)_2OCH_3COONaNaOC_2H_5$ gave off alcohol when heated, but this observation is of little weight in favor of the theory, since the substance at the same time underwent a far-reaching decomposition, of which the alcohol may have been a product, instead of being alcohol of crystallization.

[3] Compt. rend., **121**, 530 (1895).　　　　[4] This JOURNAL, **20**, 426.

to the class of compounds discussed in this paper, and, if this connection can be proved, would show that the alcoholate is added to carbon and not to the nitro group. In continuing work in this direction an attempt will be made to find such substances not derived from quinones, as in quinones a special method of attachment of sodic alcoholate is possible, forming the hemiacetals. This line of work will be pursued in this laboratory during the coming year. It is worth mentioning that Astre independently of Victor Meyer explained the constitution of his compounds by supposing that the hydrogen on the quinone ring had been replaced by potassium, thus $C_6H_3KO_2C_2H_5OH$, a hypothesis which is inadmissible, as our derivative from chloranil undoubtedly belongs to the same class, and here $(C_6Cl_4O_2NaOCH_3)$ no such arrangement of the atoms is possible. The details of this argument will be found in the paper by H. A. Torrey and one of us, already mentioned.

By the decomposition of the corresponding colored compounds with an acid the following new picric ethers were obtained:

$C_6H_2(NO_2)_3OC_3H_7$, melting-point 43° ;
$C_6H_2(NO_2)_3OC_5H_{11}$, melting at 68°–69° ;

this was made from ordinary isoamyl alcohol; and

$C_6H_2(NO_2)_3OCH_2C_6H_5$, melting at 115°.

EXPERIMENTAL PART.

Action of Sodic Methylate on Picryl Chloride.

When a concentrated solution of picryl chloride in methyl alcohol was mixed with an excess of sodic methylate also dissolved in methyl alcohol, a mass of beautiful scarlet needles was formed immediately; or, if the solution was dilute, these scarlet needles appeared only upon standing. We first prepared the substance for analysis only by washing with water, in which it is but slightly soluble, and drying on a porous plate. The analysis of this preparation is numbered I. A second portion, after being washed with water, was recrystallized from methyl alcohol, which partially decomposed it, as

white plates of trinitranisol could be distinguished mixed with the scarlet prisms of the new body. This impurity was removed by washing with benzol, in which the scarlet compound is nearly insoluble, but the trinitranisol very soluble. This preparation dried *in vacuo* was analyzed with the result numbered II.

The scarlet compound formed according to Clemm,[1] when a solution of picryl chloride in methyl alcohol was treated with sodic hydrate, was also prepared, and gave, on analysis, the result numbered III., which proves that it is identical with the product obtained by the action of sodic methylate.

I. 0.5280 gram of the substance gave, after decomposition with sulphuric acid, 0.1168 gram of sodic sulphate.

II. 0.3518 gram of the substance gave 0.0857 gram of sodic sulphate.

III. 0.1618 gram of the substance gave 0.0410 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OCH_3NaOCH_3$.	I.	Found. II.	III.
Sodium	7.69	7.17	7.89	7.90

The formula $C_6HNa(NO_2)_3OCH_3$ requires 8.68 per cent. of sodium.

These results indicate that the substance is formed by the addition of 1 molecule of sodic methylate to 1 molecule of trinitranisol. The sodic chloride, which must have been the other product of the reaction, was removed by washing with water in the preparation of the substance.

As, according to the theory proposed by Victor Meyer, this substance must contain a molecule of methyl alcohol of crystallization,

$$(C_6HNa(NO_2)_3OCH_3CH_3OH),$$
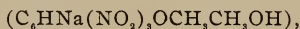
we next studied the effect of heat upon it. A sample dried for twenty-four hours *in vacuo* was heated to 100°–110°. After one hour's heating it had lost 0.0002 gram, and upon further heating remained constant. The heat was then increased to 130°–140°, but even at this temperature there was no loss in weight. In view of this experiment it seems im-

[1] J. prakt. Chem. [2], **1**, 156.

possible to maintain that the substance contains methyl alcohol of crystallization. When the temperature was raised to 165°, the substance decomposed, as was shown by a change in color.

Properties of the Addition-product of Trinitranisol and Sodic Methylate.—It crystallizes from methyl alcohol (with slight decomposition) in prisms apparently belonging to the monoclinic system, of a beautiful scarlet, or perhaps, rather vermilion, color with a bronze reflex. It decomposes at about 165°, and, if heated in the free flame, explodes with great violence. In the dry state it is comparatively stable, keeping well even when exposed to the air; but in contact with water it is gradually decomposed, forming trinitranisol, which, if the action is very long continued, passes into picric acid. Methyl alcohol dissolves it, but not without decomposition, as some trinitranisol is found mixed with the crystals obtained from such a solution; it is almost insoluble in benzol. Acids decompose it at once, forming a body, which after recrystallization from alcohol, melted at 64° and was therefore evidently trinitranisol; methyl alcohol was also set free, as shown by the odor.

Action of Ethyl Alcohol on the Addition-product of Trinitranisol and Sodic Methylate.

This work was undertaken in the hope of deciding whether the addition-product contained methyl alcohol of crystallization, as in that case the methyl alcohol must be replaced by ethyl alcohol upon recrystallization from this solvent, whereas, if the second methyl group was not present in alcohol of crystallization, it might either remain in the compound under these conditions, or be replaced by the ethyl group. If, therefore, the methyl compound were unaltered by crystallization from ethyl alcohol, it could not contain methyl alcohol of crystallization. Unfortunately, the experiment showed that the methyl group was replaced by ethyl, and therefore no inference in regard to the constitution of the body could be drawn from this work.

On recrystallizing the methyl compound from ethyl alcohol a substance was obtained closely resembling the original

methyl compound in color, crystalline form, and properties, but which gave the following result on analysis after having been dried *in vacuo* :

0.3012 gram of the substance gave 0.0681 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OC_2H_5NaOC_2H_5$.	Found.
Sodium	7.23	7.32

This result seems to indicate that the body is the ethyl compound, but is not conclusive, as the difference between the percentages of sodium in the methyl and ethyl compounds is only 0.46 per cent., and the experimental error may well reach or even exceed this amount in the case of compounds which are so hard to purify on account of their instability. But we do not have to depend on the analysis in this case, as upon decomposing the substance with an acid, and recrystallizing the product from alcohol, long, nearly colorless needles were obtained, which melted at 78°–79°, and were, therefore, the ethyl ether of picric acid. We hope that further experiments in this direction will be tried in this laboratory during the coming year.

An attempt to make this ethyl compound direct from sodic ethylate and picryl chloride did not lead to the desired result; a mass of red crystals was formed, to be sure, but these dissolved, when treated with water, to wash out the sodic chloride, giving a red solution, which gradually turned yellow, and then deposited needles of ethyl picrate.

Action of Sodic Propylate on Picryl Chloride.

A concentrated solution of picryl chloride in benzol was mixed with an excess of sodic propylate dissolved in a little propyl alcohol; a heavy precipitate of red needles was formed, which was washed thoroughly at first with benzol and afterward with water. It was then dried on a porous plate, and at last at 110°, when the following results were obtained on analysis :

I. 0.2960 gram of the substance gave, on combustion,[1] 0.4390 gram of carbonic dioxide and 0.1260 gram of water.

[1] The substance was mixed with chromic oxide to decompose the sodic carbonate formed.

II. 0.6223 gram of the substance gave 0.1235 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OC_3H_7,NaOC_3H_7$.	I.	II.
		Found.	
Carbon	40.79	40.45	....
Hydrogen	4.53	4.73	....
Sodium	6.54	....	6.44

The formula $C_6HNa(NO_2)_3OC_3H_7$ requires 36.85 per cent. of carbon, 2.73 of hydrogen, and 7.85 of sodium.

Properties of the Addition-product of Propyl Picrate and Sodic Propylate.—It resembles the methyl compound closely, but its color is a somewhat lighter red, and it is not quite so stable when exposed to the air. Acids decompose it giving propyl alcohol, recognized by the smell, and the propyl picrate, which has not been described heretofore. Propyl picrate crystallizes in fine, nearly colorless needles, melting at 43°, and is easily soluble in all the common solvents. If allowed to stand with water or an acid, it is decomposed with the formation of picric acid.

Action of Sodic Isoamylate on Picryl Chloride.

A benzol solution of picryl chloride was mixed with an excess of sodic isoamylate dissolved in a little isoamyl alcohol, and the amorphous orange precipitate formed was washed thoroughly with benzol and afterward with water, and dried at first on a porous plate finally at 110°, when it gave the following results on analysis :

0.2894 gram of the substance gave 0.0490 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OCH_6H_{11}NaOC_6H_{11}$.	Found.
Sodium	5.62	5.48

The formula $C_6HNa(NO_2)_3OC_6H_{11}$ requires 7.16 per cent. of sodium.

Properties of the Addition-product from Isoamyl Picrate and Sodic Isoamylate.—This substance forms an orange amorphous mass, which is decomposed by all the liquids which dissolve it, so that we could not try to crystallize it. It is essentially insoluble in water or benzol. Acids decompose it, setting free isoamyl alcohol, recognized by its smell, and isoamyl picrate.

Isoamyl Picrate, $C_6H_2(NO_2)_3OC_5H_{11}$.

This substance was obtained by the action of an acid on the addition-product just described. It was purified by crystallization from alcohol, until it showed the constant melting-point 68°–69°, when it was dried *in vacuo*, and analyzed with the following result :

0.1311 gram of the substance gave, on combustion, 0.2117 gram of carbonic dioxide and 0.0558 gram of water.

	Calculated for $C_6H_2(NO_2)_3OC_5H_{11}$.	Found.
Carbon	44.14	44.02
Hydrogen	4.34	4.73

Isoamyl picrate crystallizes from alcohol in nearly colorless hexagonal plates, which melt at 68°–69°. It is decomposed by standing with water or acids, but in this respect is much more stable than propyl picrate.

Action of Sodic Benzylate on Picryl Chloride.

When picryl chloride in benzol solution was treated with an excess of sodic benzylate, a mass of beautiful red needles was formed, which, after washing thoroughly with benzol and water, was dried on a porous plate, and afterward at 110°, and analyzed with the following result :

0.3125 gram of the substance gave 0.0470 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OC_7H_7NaOC_7H_7$.	Found.
Sodium	5.12	4.87

The formula $C_6HNa(NO_2)_3OC_7H$ requires 6.74 per cent. of sodium.

Properties of the Addition-product of Benzyl Picrate and Sodic Benzylate.—This substance crystallizes in red needles of a somewhat lighter shade than the propyl compound, and shows a distinct fluorescence. It is also more stable than the propyl compound, since a sample of it stood exposed to the air in a watch-glass for some months without any visible change. Water decomposes it, but much more slowly than the other compounds of this class. In this decomposition, as well as in that by an acid, the principal products are benzyl alcohol and benzyl picrate.

Benzyl Picrate, $C_6H_2(NO_2)_3OC_7H_7$.

This substance, prepared by the action of an acid on the addition-product just described, was purified by recrystallization from alcohol, until it showed the constant melting-point 115°, when an analysis gave the following result :

0.3828 gram of the substance gave, on combustion, 0.6805 gram of carbonic dioxide and 0.1090 gram of water.

	Calculated for $C_6H_2(NO_2)_3OC_7H_7$.	Found.
Carbon	48.90	48.48
Hydrogen	2.82	3.16

Benzyl picrate crystallizes from alcohol, in which it is difficultly soluble, in nearly colorless plates, melting at 115°. It is gradually decomposed by acids, forming picric acid.

Action of Baric Hydrate on Picryl Chloride, or on Trinitranisol in Methyl Alcoholic Solution.

When a concentrated solution of picryl chloride in methyl alcohol was treated with an excess of an aqueous solution of baric hydrate, a dense mass of red crystals was formed, which were collected, and washed with water as quickly as possible to prevent the formation and precipitation of baric carbonate from the excess of baric hydrate. The crystals were then dried on a porous plate. Trinitranisol dissolved in methyl alcohol gives the same compound, when treated with aqueous baric hydrate, and as thus a purer product was obtained, we prepared most of our material in that way. Analysis of the air-dried substance gave the following result :

0.8154 gram of substance gave 0.2394 gram of baric sulphate.

	Calculated for $[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2.10H_3O$.	Found.
Barium	16.37	17.26

As this indicated that the substance contained water of crystallization, its behavior when heated was studied.

I. 0.7733 gram of the air-dried substance lost 0.1622 gram at 110°–130°.

II. 0.3513 gram of the air-dried substance lost 0.0736 gram at 110°–130°.

III. 0.8206 gram of the air-dried substance lost 0.1738 gram at 110°–130°.

	Calculated for $[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2.10H_2O.$	I.	Found. II.	III.
Water	21.50	20.97	20.95	21.17

I. 0.4064 gram of the substance dried at 110°–130° gave 0.1504 gram of baric sulphate.

II. 0.4616 gram of the substance gave 0.1694 gram of baric sulphate.

III. 0.1296 gram of the substance gave, on combustion, 0.1201 gram of carbonic dioxide[1] and 0.0259 gram of water.

IV. 0.2654 gram of the substance gave[2] 31.4 cc. of nitrogen under a pressure of 753.1 mm. and at a temperature of 20°.5.

	Calculated for $[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2.$	$[C_6H(NO_2)_3OCH_3]_2Ba.$	I.	II.	III.	IV.
Ba	20.85	22.05	21.76	21.58	....	....
C	25.56	27.05	....	....	25.26	....
H	1.83	1.29	....	....	2.22	....
N	12.78	13.53	....	....	....	13.40

These results, therefore, do not decide with certainty between the two formulas, for, although the percentage of carbon speaks strongly in favor of $[C_6H_2(NO_2)_3OCH_3]_2BaO_2H_2$, the determinations of barium agree with the percentage calculated for the second formula. As the most probable impurity in the substance was baric carbonate, we shall provisionally adopt the formula containing baric hydrate.

Properties of the Addition-product of Trinitranisol and Baric Hydrate.—It forms needles of a fine red color verging toward scarlet. When heated to 110°, it loses its water of crystallization, and turns a beautiful dark crimson, but the dried salt absorbs water very eagerly from the air, regaining its scarlet-red color. This fact necessitates great care in handling the dried salt during the process of analysis. Part, but not all, of the water of crystallization is given off *in vacuo*. It is insoluble in water. Acids decompose it, giving trinitranisol, but no alcoholic odor was observed.

[1] Chromic oxide was used to decompose the baric carbonate formed. The substance was spread out in a long copper boat, and heated very carefully to avoid explosions.

[2] The substance was mixed with sand to decompose any baric nitrite which might have been found.

Calcic hydrate added to a solution of picryl chloride in methyl alcohol gave a red precipitate, but this decomposed almost immediately with formation of trinitranisol. Dinitranisic acid dissolved in methyl alcohol gave a magnificent purple coloration, when treated with aqueous baric hydrate, but the substance formed was very unstable. It is mentioned here, as it forms an additional argument for classing the trinitranisol compounds described in this paper with the colored derivatives of dinitranisic acid discovered by Ittner and one of us.

The work will be continued in this laboratory.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

XIV.—ON THE ACTION OF ORTHODIAZOBENZENESULPHONIC ACID ON METHYL AND ETHYL ALCOHOL.[1]

BY E. C. FRANKLIN.

Preparation of Ortho- and Metamidobenzenesulphonic Acid.

As the two acids were obtained in considerable quantity and by a method somewhat different from that employed by Limpricht[2] and that employed by Shober and Kiefer,[3] an account of the method is here given.

Preparation of the Nitrosulphonic Acids.—250 grams of pure benzene and 300 cc. of fuming sulphuric acid were introduced into a flask of 1 liter capacity provided with a cork into which is fitted a long glass tube to serve as a reflux condenser. The reaction began at once, accompanied by considerable evolution of heat. The action was assisted by shaking, care being taken not to allow it to proceed so rapidly as to raise the temperature of the mixture to the boiling-point of benzene. At the expiration of about an hour the benzene had almost completely passed into solution. A small quantity which persistently resisted the action of the acid was removed

[2] Ann. Chem. (Liebig), **177**, 61.   [3] This JOURNAL, **17**, 454.

by transferring the acid mixture to a flask of such size that the acid mixture filled it well up into the neck. After standing a short time the benzene collected in the neck of the flask and was removed by means of a pipette. The solution of benzenesulphonic acid was then returned to the larger flask and treated with fuming nitric acid of specific gravity of 1.50. The nitric acid was added very cautiously. At the beginning of the operation the reaction was so violent that it was necessary to suspend the operation from time to time, and cool the mixture by immersion in cold water. Towards the end of the operation the action became much less violent, and finally when the addition of a considerable quantity of acid produced no further elevation of temperature the nitration was considered finished. The acid mixture was then poured into a large quantity of water and allowed to stand until a small quantity of dinitrobenzene which had been formed, had subsided. The clear yellow liquid was then decanted and neutralized with chalk. The solution was filtered from gypsum and excess of chalk, and the calcium salts converted into the potassium salts by the addition of potassium carbonate. On filtering off the calcium carbonate, a bright yellow solution of the potassium salts was obtained. The nitro acids might at this stage have been reduced to the amido acids and these subsequently separated, but after several attempts at this method, it was found advisable first to separate the nitro acids from the solution and then effect their reduction in solutions free from nitric acid. If the reduction is effected in the solution containing nitrates, a black solution results, from which the amido acids can be but very imperfectly separated. The solution of the potassium salts was concentrated and set aside to crystallize. The first crops were almost pure potassium metanitrobenzenesulphonate. They were reserved and reduced separately, furnishing pure metamidobenzenesulphonic acid, while the latter crystallizations, which were mixtures of all three modifications, were reduced without separation from each other, furnishing a mixture of the three amidobenzenesulphonic acids.

Reduction of Metanitrobenzenesulphonic Acid.—The reduc-

tion can be readily effected, either by the use of tin and hydrochloric acid or by ammonium sulphide. Limpricht used ammonium sulphide, which has also in this investigation been found preferable to tin and hydrochloric acid.

The potassium salt was dissolved in water by the aid of heat, and the solution made strongly alkaline by the addition of ammonium hydroxide. Into the solution thus prepared hydrogen sulphide was conducted until complete saturation had taken place. The solution was then heated on a water-bath until the excess of ammonium sulphide was completely expelled. Hydrochloric acid was then added, the solution filtered from separated sulphur, and set aside to crystallize. After standing over night the acid separated. By re-solution of the crude acid in boiling water and treatment with bone-black, a colorless solution was obtained, which, when allowed to stand, furnished the crystallized acid in pure condition.

Metamidobenzenesulphonic acid was thus obtained in the form of slender, colorless needles without water of crystalliza-tion. It is difficultly soluble in cold water, more readily in hot. It becomes discolored by exposure, and decomposes without melting upon being heated.

Reduction of the Mixture of the Ortho-, Meta-, and Paranitro-benzenesulphonic Acids, and the Separation and Purification of the Orthoamido Acid.—The mixture of the potassium salts of the three isomeric acids, obtained as described above, was treated with ammonium hydroxide and hydrogen sulphide. The acid solution, after separation of the sulphur, was boiled with bone-black and set aside to crystallize. By proper regulation of the concentration of the solution the three amido acids crystallized out, each in its characteristic form. The meta modification was deposited as slender needles; the ortho in large, transparent, rhombohedrons which were anhydrous, while the para acid formed thick, leaf-like crystals with water of crystallization. From the crystalline mixture thus obtained, the light, slender crystals of the meta acid were re-moved, by washing, from the larger and heavier crystals of the isomeric acids. The remaining mixture of the ortho and para acids was then partially dried by pressure between folds

of absorbent paper, and the desiccation completed in the air-bath at a temperature of 110°–120°, by which treatment the para acid lost its water of crystallization and crumbled to powder. The anhydrous ortho acid was not affected, and was separated from the pulverulent para acid by means of a sieve. The ortho acid was then, after several recrystallizations from hot water and treatment with bone-black, obtained in pure condition.

In one experiment a yield of over four per cent. was obtained. Other experiments were less satisfactory.

Orthoamidobenzenesulphonic acid was thus obtained in fine crystals of a rhombohedral habit, and usually of a pronounced pink color. It is difficultly soluble in cold water, more readily in hot water, and decomposes without melting on being heated.

The paramidobenzenesulphonic acid from the above mixture was purified by recrystallization, and its identity with sulphanilic acid, prepared by the action of sulphuric acid on aniline, was confirmed. A small quantity of the acid was diazotized, the diazo compound decomposed with methyl alcohol, and the resulting methoxybenzenesulphonic acid converted into the amide. This amide,[1] $C_6H_4\begin{smallmatrix}OCH_3\\SO_2NH_2(b)\end{smallmatrix}$, crystallized in colorless, well-formed needles melting at 112°.

Preparation of Orthodiazobenzenesulphonic Acid.

An excellent yield of the diazo compound was obtained by suspending the amido acid in ordinary alcohol and passing a stream of nitrous fumes into the mixture. The reaction takes place with remarkable ease.

Ten grams of the finely powdered amido acid were suspended in 25 cc. ordinary alcohol and a rapid stream of nitrous fumes passed into the mixture. The contents of the flask became warm, but the temperature was not allowed to rise above 40°–50°. In about ten minutes the reaction was complete. An equal volume of ether was then added to the

[1] Shober : This JOURNAL, **15**, 380.

mixture, and the flask with its contents left at rest in a freezing-mixture of ice and salt for several hours. The diazo compound was then filtered off, washed with ether, and spread out on filter-paper to dry. A yield of 10 grams was obtained. Orthodiazobenzenesulphonic acid thus prepared is a beautiful, white, crystalline powder, which slowly becomes colored on exposure. It is comparatively stable and if protected from air and moisture it can be kept for a considerable time without suffering appreciable change. It explodes by contact with flame or by percussion.

The Relative Susceptibility of the Ortho-, Meta-, and Paramidobenzenesulphonic Acids to the Action of Nitrous Acid.

It is interesting to compare, in passing, the relative susceptibilities of the three isomeric amidobenzenesulphonic acids to the action of nitrous acid. Metamidobenzenesulphonic acid cannot be satisfactorily diazotized by treatment in suspension in alcohol with nitrous fumes, as the author has found by repeated trials. Suspended in water, however, it is diazotized without the least difficulty. The paramidobenzenesulphonic acid must, according to Shober,[1] be very finely powdered. When this preliminary has been properly attended to, a quantity of the acid suspended in alcohol can be diazotized in from one to two hours. It has been determined in the present investigation that the para acid is diazotized with much more difficulty under the above conditions than is the ortho acid. Mr. Daniel Base, working in this laboratory, found it quite impossible to effect complete transformation of sulphanilic acid by this method. There always remained behind, when the diazo acid was decomposed, a residue of sulphanilic acid. The remarkable ease with which the ortho acid can be diazotized under these conditions is evident from the description of its preparation above. Similar relations between the paratoluidineorthosulphonic acid and the paratoluidinemetasulphonic acid have been pointed out by Metcalf.[2] The latter compound in which the amido and sulphonic acid groups occupy the ortho position relatively to each other, is readily diazotized by suspension in alcohol, while the for-

[1] Dissertation, 1892, p. 7.   [2] This JOURNAL, **15**, 305.

mer acid, in which these two groups occupy the meta position relatively to each other, cannot satisfactorily be so diazotized. It is, of course, recognized that difference of solubility of the amido compounds may account for their observed behavior when suspended in alcohol.

Decomposition of Orthodiazobenzenesulphonic Acid with Methyl Alcohol.

1. *At Atmospheric Pressure.*—Three grams of the diazo compound and 25 cc. methyl alcohol were heated in a flask with reflux-condenser. The reaction was complete in twenty minutes, yielding a clear and but slightly colored solution. The decomposition-products were treated in the usual manner for the amides. 0.8 gram of pure methoxybenzenesulphonamide, melting at 171°, was obtained, while no benzenesulphonamide could be found. The amides in every case of decomposition of the ortho acid were found to be less contaminated with the gummy impurities than were the decomposition-products of the meta acid.

2. *At Atmospheric Pressure + 850 mm. of Mercury.*—Three grams of the diazo compound, together with 100 cc. methyl alcohol, were introduced into the pressure-flask[1] and the decomposition carried out at the above indicated pressure. The reaction was complete in five minutes, furnishing a clear and but slightly colored solution. The alcohol was removed by distillation, and the residue treated as usual for the amides. Only the methoxybenzenesulphonamide, melting at 171°, could be identified.

3. *At Atmospheric Pressure — 450 mm. of Mercury.*—Five grams of the diazo compound, together with 60 cc. methyl alcohol, were introduced into the flask of the apparatus for decomposition at diminished pressure,[2] and after adjustment of the pressure, the contents of the flask were heated to boiling. The solution slowly took on a light-red color, and after about seven hours' boiling the decomposition was complete. The alcohol was removed by distillation, and the residue treated as in the foregoing experiments for the amides. 1.54 grams of methoxybenzenesulphonamide, melting at 171°, was ob-

[1] Remsen and Palmer: This JOURNAL, 8, 245.　　[2] Parks: This JOURNAL, 15, 324.

tained, while from the mother-liquors no benzenesulphon-
amide could be separated.

Orthomethoxybenzenesulphonamide crystallizes in colorless
needles which are but sparingly soluble in cold water, more
readily soluble in hot water or in alcohol.

A determination of sulphur in the amide obtained in these
experiments resulted as follows : 0.2242 gram of the substance
gave 0.2777 gram barium sulphate, which corresponds to
17.04 per cent. sulphur. The percentage of sulphur calcula-
ted for $C_6H_4(OCH_3)(SO_2NH_2)$ is 17.11.

Further proof of the identity of this compound was fur-
nished by chlorine and sulphur determinations in the ortho-
methoxybenzenesulphone chloride, which compound has also
been prepared by Haitinger.[1]

Preparation of Orthomethoxybenzenesulphone Chloride.—Fif-
teen grams of orthodiazobenzenesulphonic acid were decom-
posed with 125 cc. methyl alcohol at a pressure of 850 mm.
above atmospheric pressure. The reaction was complete in
forty-five minutes, furnishing as a product a clear and but
slightly colored solution. The acid liquid was neutralized
with pure barium carbonate and the attempt made to obtain
a pure barium salt. A quantity of crystals were obtained
which were in all probability the impure barium salt. This
was not further studied, as it seemed more desirable to use
the material for the preparation of the chloride. The barium
salt was changed into the potassium salt, and this, by the
usual method with phosphorus pentachloride, was converted
into the acid chloride. As noticed when working with
smaller quantities in the experiments above, this chloride
separated from the reaction-mixture, on treatment with water,
as a waxy solid. It was washed with water and dissolved in
ether. The ethereal solution was dried with calcium chloride,
filtered, and placed in a desiccator to crystallize. From the
concentrated solution the chloride separated in nearly colorless
plates, which upon recrystallization from petroleum ether
(b. p. below 100°) was deposited as stout needles. It was found
to melt at 56°. Haitinger[2] prepared this chloride from ortho-
phenolsulphonic acid and found its melting-point to be 55°.

[1] Monatsch., 4, 173.   [2] *Loc. cit.*

Determinations of chlorine and sulphur in this compound gave the following results:

I. 0.2266 gram of the substance gave 0.1585 gram silver chloride, which corresponds to 17.29 per cent. chlorine. The percentage of chlorine calculated for $C_6H_4(OCH_3)(SO_2Cl)$ is 17.19.

II. 0.2030 gram of the substance gave 0.2335 gram barium sulphate, which corresponds to 15.81 per cent. sulphur. The percentage of sulphur calculated for $C_6H_4(OCH_3)(SO_2Cl)$ is 15.50.

Decomposition of Orthodiazobenzenesulphonic Acid with Ethyl Alcohol.

1. *At Atmospheric Pressure.*—Five grams of the diazo compound and 75 cc. ethyl alcohol were decomposed as usual. In from five to seven minutes the decomposition was completed. The resulting light-red colored solution was treated in the usual manner for the amides. The only amide obtained was an ethoxybenzenesulphonamide, melting at 156°.

2. *At Atmospheric Pressure + 850 mm. of Mercury.*—Five grams of the diazo compound, together with 75 cc. ethyl alcohol, were introduced into the pressure-flask and the decomposition initiated under full pressure, but because of an accident it was completed at atmospheric pressure. 0.75 gram of the pure ethoxybenzenesulphonamide, melting at 156°, was obtained.

Whether or not the hydrogen reaction takes place in these decompositions could not be definitely determined from the above experiments. The melting-points of the two compounds, orthoethoxybenzenesulphonamide and benzenesulphonamide, lie so near together that determinations of these constants could not be made use of as guides. Repeated attempts to obtain crops of mixed crystals of different habit, from the mother-liquors, were unsuccessful. This, together with the fact that the amide obtained showed a constant melting-point, led to the conclusion that the hydrogen reaction did not take place.

A sulphur determination resulted as follows: 0.2203 gram of the substance gave 0.2547 gram barium sulphate, which

corresponds to 15.89 per cent. sulphur. The calculated percentage of sulphur in $C_6H_4(OC_2H_5)(SO_2NH_2)$ is 15.92.

Orthoethoxybenzenesulphonamide crystallizes from hot dilute alcohol as colorless, slender needles. It is almost completely insoluble in cold water, and but sparingly soluble in hot water.

G. T. Moody[1] prepared the orthoethoxybenzenesulphonamide by the ethylation of parabromphenol, sulphonation of the bromphenetol thus formed, reduction of the bromphenetolorthosulphonic acid, and conversion of the resulting acid into its amide. He found its melting-point to be 156°.

Action of Fuming Nitric Acid on Alkoxybenzenesulphonamides.

1. *On Paramethoxybenzenesulphonamide.*—Shober[2] has shown that when paramethoxybenzenesulphonamide is treated with nitric acid metadinitrobenzene is formed. It was thought desirable to study this reaction somewhat further, and also to study the action of nitric acid on the ortho and meta amides. That metadinitrobenzene is not the only product of the action of nitric acid on this amide was suspected because of the small yield of the nitro product obtained. In order to determine what other compounds might be formed 4.4 grams paramethoxybenzenesulphonamide were added gradually to 10 grams of fuming nitric acid, of specific gravity 1.52, kept cold by a freezing-mixture of ice and salt. It was observed that when the temperature of the acid was kept well down the quantity of metanitrobenzene formed was always much decreased. The acid liquid was diluted with water, which caused a separation of a small quantity of dinitrobenzene. This was filtered off, and the filtrate evaporated with alcohol for the purpose of removing the excess of acid. The thick syrupy residue was diluted with water and neutralized with potassium hydroxide, when immediately a crop of crystals of the potassium salt of an acid of the composition given below was obtained :

The analysis of the compound yielded the following results :

I. 0.3498 gram gave 0.4021 gram carbon dioxide and 0.0751 gram water.

[1] J. Chem. Soc., 1892-93, 214.   [2] This JOURNAL, 15, 390.

II. 0.2854 gram gave 13.9 cc. nitrogen measured over water at a temperature of 18°, and 726 mm. barometric pressure.

III. 0.1265 gram gave 0.1127 gram barium sulphate.

IV. 0.1448 gram gave 0.0467 gram potassium sulphate.

	Calculated for $C_7H_6O_6NSK$.	I.	Found. II.	III.	IV.
C	31.00	31.34	....	....	....
H	2.21	2.38	....	....	....
N	5.17	....	5.31	....	....
S	11.81	....	....	12.23	....
K	14.38	....	....	....	14.46

The principal product of the action of nitric acid on paramethoxybenzenesulphonamide is hence a mononitroparamethoxybenzenesulphonic acid of the formula :

$$C_6H_3 \begin{cases} NO_2 & (?) \\ OCH_3 & (1) \\ SO_2OH & (4) \end{cases}$$
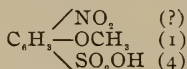
A portion of this acid was reduced to the amido compound, while another was converted into the sulphonamide by successive treatment with phosphorus pentachloride and ammonium hydroxide. The sulphonamide was obtained as well-formed, yellow needles melting at 138°–140°.

2. On Metamethoxybenzenesulphonamide.—Three grams of the amide were added gradually to 10 grams of fuming nitric acid. The experiment was carried out as nearly as possible in the same manner as described for the corresponding para compound. No dinitrobenzene was obtained.

A second experiment, in which 5 grams of the amide and 20 grams of the acid were used, also failed to give any dinitrobenzene. The solutions from these two experiments were united, and evaporated with alcohol to remove the excess of nitric acid. The residue was taken up with water and neutralized with barium carbonate. The filtered solution, after boiling with bone-black and concentration, deposited crystals of a barium salt of a nitrosulphonic acid. This salt deflagrated when heated on platinum foil, and a test for sulphur showed it to contain this element.

3. On Orthomethoxybenzenesulphonamide.—One gram of the

amide was added to 4 grams of fuming nitric acid as in the previous experiments. Upon dilution a small quantity of yellow needles of metadinitrobenzene, melting at 88°, crystallized out.

4. *On Paraethoxybenzenesulphonamide.*—Two and one-half grams of the amide, added as in the above experiments to 10 grams of fuming nitric acid, gave on dilution a considerable yield of dinitrobenzene. This substance, after being once recrystallized from dilute alcohol, melted at 83°–84°.

Table Showing the Results of the Decompositions of the Diazo-benzenesulphonic Acids with

1. *Methyl Alcohol.*

	At atmospheric pressure — 450 mm. mercury	At atmospheric pressure.	At atmospheric pressure + 850 mm. mercury
Ortho acid	Methoxy[3]	Methoxy	Methoxy
Meta acid[1]	{ Methoxy { Hydrogen	{ Methoxy { Hydrogen	Methoxy
Para acid[2]	Hydrogen	{ Hydrogen { Methoxy	{ Methoxy { Hydrogen

2. *Ethyl Alcohol.*

	At atmospheric pressure.	At atmospheric pressure + 850 mm. mercury.
Ortho acid	Ethoxy	Ethoxy
Meta acid[1]	{ Ethoxy { Hydrogen	{ Ethoxy { Hydrogen
Para acid[2]	Hydrogen	Hydrogen

Conclusion.

The more important results reached in this investigation may be summarized as follows :

1. When orthodiazobenzenesulphonic acid is decomposed with methyl alcohol the methoxy product only is obtained.

2. When the decomposition of orthodiazobenzenesulphonic acid is effected with ethyl alcohol the alkoxy reaction only takes place.

3. Higher pressures favor the alkoxy reaction.

[1] Shober and Kiefer ; This JOURNAL, **17**, 454.
[2] Shober : This JOURNAL, **15**, 379.
[3] Large type signifies large yield; small type signifies smaller yield.

4. The yield of the alkoxyamide is greater when the decomposition of the diazo compound is made with the simpler alcohol.

5. When paramethoxy- or paraethoxybenzenesulphon-amide is treated with fuming nitric acid one of the products is metadinitrobenzene. At the same time a nitro substitution-product of paramethoxybenzenesulphonic acid is formed.

6. When metamethoxybenzenesulphonamide is treated with fuming nitric acid, no metadinitrobenzene is formed.

7. When orthomethoxybenzenesulphonamide is treated with fuming nitric acid one of the products formed is metadinitrobenzene.

ON THE TASTE AND AFFINITY OF ACIDS.

By J. H. Kastle.

Quite recently Richards[1] has shown that, qualitatively at least, a definite relation exists between the sour taste of acids and the extent of their dissociation, and he has succeeded in proving that the sense of taste might be employed in the laboratory with far greater precision than has hitherto been thought possible. In 1893, it also occurred to the writer that there might be some connection between the degree of sourness of acids and their chemical affinity, and accordingly an investigation of the subject was then undertaken in which the taste of nineteen acids was compared on sixteen different individuals. About 400 observations were made and recorded. Other matters became pressing, however, and the investigation was left in just the shape in which it is here presented, the idea being to take it up again when the opportunity offered. While this opportunity never presented itself it is believed that the results reached at that time are of sufficient interest, especially in the light of the recent developments of the subject, to warrant the following discussion. It should be observed in this connection that no claim of priority is made either directly or indirectly, and no interference with the work of others is intended. It is believed, however, that a good deal of evidence has been collected by the writer, inde-

[1] This JOURNAL, **20**, 121.

pendently, which has an important bearing on the question concerning the relation between the taste of acids and their strength, and in the following this is given simply for what it is worth.

As the result of some preliminary work, it was found that a dilution of $\frac{1}{50}$ normal was likely to prove best suited for the purpose of comparison. Nineteen acids of this dilution were used in the investigation. These were as follows : Hydrochloric, nitric, hydrobromic, sulphuric, benzenesulphonic, iodic, propionic, monochloracetic, acetic, formic, glycolic, lactic, malonic, oxalic, citric, phthalic, malic, succinic, and tartaric. In order to do away, as largely as possible, with any individual idiosyncrasies relative to the sense of taste, it was thought advisable to make the comparisons on as large a number of individuals as practicable. Sixteen persons, besides the writer, kindly allowed the necessary tests to be made upon them. These were as follows : H. H. Hill, Clara Shaw, Anne May, Mary McCann, Irvine Lyle, R. L. Weaver, W. J. Calvert, A. M. Peter, M. A. Scovell, F. P. Anderson, Henry Curtis, H. Garman, Alice Shelby, H. S. Bush, C. W. McElroy, S. E. Bennett. I take this opportunity to thank them for their kindness in the matter.

In conducting the tests equal amounts of the two acids being compared, usually about 1 cc., were placed one after the other on the tongue of the observer, allowing sufficient time for the taste of the first acid to disappear before bringing the second one on the tongue. The person on whom the test was made was then asked to decide which acid was the sourer of the two. It occasionally happened, though not often, that the person would wish to taste the two acids several times in succession, and in different order, before venturing an opinion concerning their relative sourness.

In consequence of the voluminousness of the results it has not been thought advisable to give them all in detail ; and in the following they are presented only in a general way.

Altogether 403 observations were made. A careful examination of these results shows that, leaving out of consideration 14 observations on the strongest acids, such as hydrochloric and

nitric,[1] etc., there are 296 comparisons in which the stronger acid was found to have the sourer taste, and only 93 in which the weaker acid was said to taste sourer. In other words, 76.09 per cent. of the observations are in support of the conclusion that a definite relation exists between the sour taste of acids and their affinity, or, as Richards[2] has expressed it, between the sour taste and their electrolytic dissociation, whereas, 23.91 per cent. of the observations are opposed to this conclusion. It should be mentioned in this connection, however, that in 157 of these observations a very strong acid was compared with a very weak one. In 126 instances the very strong acid was found to taste sourer than the very weak, whereas in 31 instances the reverse of this was found to be true; *viz.*, the very weak acid tasted sourer than the very strong one. This gives a percentage of error of 19.74—a number which differs but little from that found for all the observations; *viz.*, 23.91, so that the general character of the results would seem to be the same whether the comparisons are made between acids differing but slightly in strength, or between those differing most widely in this respect.

In view of these results, therefore, it can scarcely be doubted that some fundamental and general relation exists between the taste of acids and their affinity. The results obtained with the several members of a series of related acids are especially interesting in this connection. In the case of formic, acetic, and propionic acids the following data have been compiled from the observations :

In 11 observations formic acid was found to be sourer than acetic.

In 18 observations formic acid was found to be sourer than propionic.

In 2 observations acetic acid was found to be sourer than formic.

In 9 observations acetic acid was found to be sourer than propionic.

[1] These 14 observations on the strongest acid cannot be put in either of the two classes given in the above for the reason that all of these acids have the same strength. It matters really very little, however, whether these few observations are counted for or against the views discussed in the above.

[2] *Loc. cit.*

In 1 observation propionic acid was found to be sourer than formic acid.

In no observation was propionic acid found to be sourer than acetic.

So far, then, as the sourness is concerned, these 3 acids stand to one another in the relation formic > acetic > propionic; and, as is well known, these acids stand to one another in a similar relation as regards their chemical affinity. Similar results were obtained in the case of monochloracetic and acetic acids:

In 9 observations monochloracetic acid was found to be sourer than acetic.

In 2 observations acetic acid was found to be sourer than monochloracetic.

The coefficients of affinity of these two acids, as given by Ostwald, are for monochloracetic 0.049 and for acetic 0.00424.

So in the case of several of the common dibasic organic acids belonging to the same group we meet with differences in taste which correspond almost exactly to differences in affinity.

For example:

In 3 observations succinic acid was found to be sourer than malic.

In no observation was succinic acid found to be sourer than tartaric.

In 11 observations malic acid was found to be sourer than succinic.

In 1 observation malic acid was found to be sourer than tartaric.

In 3 observations tartaric acid was found to be sourer than succinic.

In 9 observations tartaric acid was found to be sourer than malic.

In order of taste these acids are, therefore, tartaric > malic > succinic. They are the same in order of affinity.

The following are the results obtained with glycolic and lactic acids as compared with one another and with acetic and propionic, respectively:

In 10 observations glycolic acid was found sourer than acetic.

In 6 observations glycolic acid was found sourer than propionic.

In 3 observations glycolic acid was found sourer than lactic.

In 5 observations acetic acid was found sourer than glycolic.

In no observation was acetic acid found sourer than lactic.

In 3 observations lactic acid was found sourer than acetic.

In 10 observations lactic acid was found sourer than propionic.

In no observation was lactic acid found sourer than glycolic.

In 2 observations propionic acid was found sourer than glycolic.

In no observation was propionic acid found sourer than lactic.

Here the relation glycolic > lactic > acetic > propionic is not borne out by the relative differences in taste quite so decidedly as in the other series of acids already discussed. The difference between lactic acid and propionic is clearly shown by the taste, and so possibly also is the difference between glycolic and lactic. The difference in taste between glycolic and acetic, however, is not by any means so marked; in fact there was a good deal of confusion upon this point. According to one observer, however, who was exceedingly careful in arriving at conclusions respecting differences of taste, there was no doubt that glycolic was sourer than acetic, he having reached this conclusion after repeated trials on the taste of these two acids. So that taking all of these results into consideration, it is believed that judging entirely from differences in taste one would be justified in writing these acids in the following order of strength: glycolic > lactic > acetic > propionic.

In conclusion, it should be observed that the sour taste of acids is characteristic of a larger number of compounds than almost any other property that could be named as distinctive of any group of substances. Almost as many acids have a sour taste as redden litmus, or exhibit electrolytic dissocia-

tion in aqueous solution. As is well known, however, there are a few compounds which redden litmus, form salts, are more or less dissociated in aqueous solution, and which are ordinarily classed among the acids, that have not a sour taste. Such compounds are, for example, picric acid and benzoic sulphinide, the former of which is intensely bitter ; the latter intensely sweet. Such instances, however, are exceedingly rare and do not seriously affect the general conditions of the problem. It would seem probable that the characteristic taste of such compounds as picric acid and benzoic sulphinide is due to the negative ion, the taste of which, in these compounds is so pronounced as to overcome that of the hydrogen ion altogether. This view derives support from the fact that the salts of such acids have the same taste as the acids themselves. The salts of benzoic sulphinide, for example, are sweet, those of picric acid are intensely bitter. In his study of the halogen substitution-products of benzoic sulphinide R. de Roode[1] observed that the calcium salts of *p*-fluor-, *p*-chlor-, *p*-brom-, and *p*-iodosulphinides have the same taste as the sulphinides themselves. On the other hand, it has been shown by Richards[2] that the *sour taste* of acids disappears completely on neutralization. The fact then that so very many acids are sour to the taste would of itself seem to indicate a close and intimate dependence of taste on the composition of this class of compounds, and if the sour taste is dependent on composition at all, then differences in composition ought at least to give rise to differences in the degree of sourness. The introduction of a strongly acidifying element or group into a weak acid, for example, ought to intensify the sour taste of the acid, in the same way, if not to the same extent, that it increases its electrical conductivity and its chemical affinity.

That such is indeed the case is shown especially in the comparisons made on the taste of monochloracetic and acetic acids, which are given in the above ; and that the order of affinity of several acids can be approximately determined at least, by the sense of taste, seems scarcely to admit of doubt.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Feb., 1898.

[1] This JOURNAL, **13**, 227.   [2] *Ibid*, **20**, 22.

THE ACTION OF NITRIC ACID ON TRIBROMACET-
ANILIDE.

By William B. Bentley.

Introduction.

The attention of the writer was directed to this subject by the conflict between the accounts of tribromnitraniline (bromine atoms symmetrically placed) published by Körner[1] and confirmed by Nölting and Collin[2] and that given by Remmers[2]. The substance was made by Körner by brominating meta-nitraniline, and the constitution was confirmed by elimination of the amido group whereby he obtained the nitrotribrombenzol described by Jackson[4], thus proving the symmetrical position of the bromine atoms, and establishing the constitution of his compound. The product described by Remmers melted at 214°–215° instead of 102°.5, as given by the other investigators, and showed in other respects very different properties from those described by Körner. According to his description of his work, he converted ordinary tribromaniline into tribrom-acetanilide by the action of acetyl chloride. This tribrom-acetanilide was then converted into tribromnitracetanilide by action of nitric acid, and this was in turn saponified by heating with aqueous or alcoholic ammonia in a sealed tube to 180°–200°. This method of preparation left no doubt that, if a tribromnitraniline had been prepared as Remmers affirmed, it must be the same as that made by Körner, inasmuch as the bromine is symmetrically placed in tribromaniline, and could hardly have been transferred by any reaction which he described. Of course, it is obvious that two tribromnitranilines cannot be derived from symmetrical tribrombenzol. One point at which error seemed most likely was the saponification of nitrotribromacetanilide with ammonia. It appeared by no means improbable that a substitution-product had been formed in this way instead of the tribromnitraniline.

In view of these facts it seemed of sufficient importance to

[1] Jsb. d. Chem., 1875, 347.   [2] Ber. d. chem. Ges., 17, 266.
[3] Ibid, 7, 351.   [4] Ibid, 8, 1172.

repeat the work of Remmers in order that the error might be detected and the facts correctly stated. In the work described below the author has found himself able to confirm less of Remmers' work than was at first expected. The tribromacetanilide was readily prepared but, though numerous methods were resorted to, a nitro derivative of this could in no way be obtained. Fuming nitric acid either had no action or produced an oily mass from which nothing crystalline was obtainable. With ordinary concentrated nitric acid (sp. gr. 1.38) several products were formed—tetrabrombenzol, a volatile oil of irritating odor (probably dibromdinitromethane), bromanil, oxalic acid and probably picric acid. If the nitric acid was dilute or was used in glacial acetic acid solution the products were the same as with concentrated nitric acid though they were apparently formed in different proportions. The only compound therefore described by Remmers which was capable of verification was tribromacetanilide.

In attempting to establish the identity of the bromanil formed by the reaction as above stated, the action of sodic phenylate was tried with the expectation of forming the dibromdiphenoxyquinone described by Jackson and Grindley[1]. The product of the reaction proved, however, to be quite different from Jackson and Grindley's compound. To make sure that this difference did not indicate that the substance used was other than bromanil this latter compound was prepared by the method of Stenhouse[2] but it gave the same compound that had been obtained before. This proves that with suitable modifications of the conditions of the reaction described by Jackson and Grindley bromanil yields a compound different from that obtained by these chemists. This compound was proved to be dibromdiethoxyquinone, a compound which is formed whenever bromanil is treated in absolute alcohol with sodic ethylate, sodic carbonate (anhydrous), potassic acetate, or oxide of silver. The difference between the conditions of the reaction described herein and the conditions of the reaction of Jackson and Grindley was found in the amount of water present, their reaction requiring the presence of water.

[1] Proc. Am. Acad.,**30**, 451.　　　　　[2] Ann. Chem. (Liebig) Suppl., **8**, 13.

Experimental Part.

Tribromacetanilide was prepared in essentially the same way as was described by Remmers. Tribromaniline was dissolved in glacial acetic acid and acetyl chloride was added in excess. The mixture was boiled under a return-condenser until there was no further evolution of hydrochloric acid. On cooling, the tribromacetanilide crystallized out very nearly pure. The yield thus obtained was about 60 per cent. of the tribromaniline taken.

Action of Fuming Nitric Acid upon Tribromacetanilide.

Tribromacetanilide was covered with fuming nitric acid and left for six weeks standing in the laboratory at ordinary temperature. At first a slight evolution of red fumes was observed and the slightly gray color of the tribromacetanilide disappeared leaving the substance colorless. No further action was evident and, at the end of the time, the undissolved matter was separated and recrystallized, when it showed the melting-point 232° and was therefore unaltered tribromacetanilide. Two portions were next taken, covered with fuming nitric acid and heated, the one for a few minutes and the other for one-half hour, when they were cooled and diluted. The one which had been heated longer yielded a yellow solution containing a small quantity of oily matter, from which no crystalline product was obtainable. The other contained a small quantity of crystalline matter in addition to the oil and yellow solution. This was separated and recrystallized, when it melted at 227°, thus proving by the melting-point as well as by the crystalline form that it was unaltered tribromacetanilide. The experiments were varied by dissolving in glacial acetic acid and treating with fuming nitric acid, but the results were precisely similar to those described above. If the action was prolonged, a red, oily, unworkable mass was obtained while, if the reaction was interrupted sooner, there was found, in addition to the other products, a small quantity of unaltered tribromacetanilide. From these experiments it was decided that fuming nitric acid gave a nitro derivative such as was described by Remmers under no conditions that could be found. It is interesting in this connection to note the re-

sults obtained by Losanitsch[1] from the action of nitric acid on tribromaniline. They may be summarized as follows: When tribromaniline is boiled with concentrated nitric acid, dibromdinitromethane distils over and tetrabrombenzol remains in the flask together with bromanil, oxalic acid, and picric acid. When nitric acid acts upon tribromaniline in glacial acetic acid solution the same products are formed; if, however, the heating of the mixture is stopped when red fumes begin to come off, dibromnitraniline is formed. The author has repeated the experiments of Losanitsch, and finds that dibromnitraniline is formed without great difficulty by heating a glacial acetic acid solution of tribromaniline with either concentrated or fuming nitric acid until the solution becomes yellow. The difference between the behavior of tribromaniline and the acetyl derivative when treated in glacial acetic acid solution with nitric acid is noteworthy, in view of the similarity of their behavior when treated with concentrated nitric acid alone.

Action of Concentrated Nitric Acid on Tribromacetanilide.

Having failed to reproduce Remmers' work with fuming nitric acid, ordinary concentrated nitric acid was next tried. The mixture was boiled, causing the evolution of dense red fumes and giving another substance of most irritating odor which, it should be observed, was also formed in smaller quantity in the experiments with fuming nitric acid above described. Small needle-shaped crystals were noticed in the neck of the flask, and the liquid was yellow and contained a yellow crystalline substance, as well as some gummy matter. A retort was then substituted for the flask, and the acid, carrying with it the volatile products of the reaction, was continuously distilled off, being renewed from time to time by the addition of fresh acid. The distilled acid contained a considerable volume of white, silky-looking crystals, and a yellow oil. This white compound, although it appeared considerable, was really but very little, and a great deal of material was used in getting sufficient for purification and analysis. Although Losanitsch obtained this compound (tet-

[1] Ber. d. Chem. Ges., **15**, 471.

rabrombenzol) from the undistilled portion, in this case such a method of procedure was not successful. After distilling for a short time, there was a gummy mass, from which tetrabrombenzol was not obtained by crystallization, but it did yield this compound by further distillation as has been said. It seemed probable that this gummy mass was chiefly undecomposed tribromacetanilide mixed with some oily decomposition-product (derived possibly from the acetyl group), which was by further treatment entirely destroyed. The distilled crystalline matter was repeatedly recrystallized from alcohol, and had the melting-point 92°. Recrystallization did not raise this melting-point. It was dried in the desiccator and analyzed with the following results :

I. 0.2321 gram of the substance gave on combustion 0.1542 gram of carbonic dioxide and 0.0141 gram of water.[1]

II. 0.1855 gram of the substance gave by the method of Carius 0.3341 gram of argentic bromide.

	Calculated for $C_6H_2Br_4$.	I.	Found. II.
C	18.27	18.12	....
H	0.51	0.67	....
Br	81.21	....	81.23

These analyses leave no doubt that the substance was tetrabrombenzol in a fair state of purity in spite of the fact that Körner[2] gives the melting-point of this substance as 98.5°. This discrepancy in the melting-point of tetrabrombenzol recalls a similar discrepancy in the melting-point of tetrabromdinitrobenzol. This substance was made by Richter[3] by action of nitric acid on tetrabrombenzol, and he gives the melting-point 227°–228° The same compound was made by Jackson and Wing[4] by action of a mixture of fuming nitric and sulphuric acids on tribromdinitrobenzol but the melting-point could not be raised above 224°. This low melting-point was attributed to the presence of a small amount of tribromtri (or

[2] Jsb. d. chem., 1875, 343.   [3] Ber. d. chem. Ges., 8, 1427.
[4] This JOURNAL, 10, 291.

di)nitrobenzol and it is possible that the low melting-point of the tetrabrombenzol is due to the same cause.

It is worth noting that these low-melting compounds were formed by similar methods, acting upon a tribrombenzol with an acid which causes decomposition.

As has been mentioned, there was also formed in the reaction just described, a yellow crystalline substance which remained after the acid had been distilled off. This compound was, however, formed only in very minute quantities and as it was found possible to modify the conditions so as to secure a fair quantity of this compound, no attempt was made to get from this reaction anything but the tetrabrombenzol already described.

Action of Dilute Nitric Acid on Tribromacetanilide.

It was found that if dilute nitric acid was used and the mixture boiled for a longer time the liquid became yellow and the same irritating odor was perceptible. Tetrabrombenzol also distilled off, but owing to its being less volatile with steam than with nitric acid or to a smaller yield of this compound in this reaction, much less of the tetrabrombenzol was obtained here. The yellow crystalline product was, however, in much larger quantity than before. Numerous experiments were made to find the conditions most favorable for the production of this yellow compound, and the following method gave the most satisfactory results : 15 grams of tribromacet-anilide was heated with 150 cc. of 80 per cent. acetic acid and 150 cc. of concentrated nitric acid (sp. gr. 1.4) was gradually added. Complete solution did not take place, but the tribromacetanilide was gradually replaced by the yellow compound in a crystalline and fairly pure condition. The yield was about 35 per cent. of the tribromace tanilide taken The compound was found to be very sparingly soluble in hot alcohol, from which it crystallizes in yellow scales which did not melt at 300°, though it sublimed as low as 260°. Bearing in mind the results obtained by Losanitsch it seemed probable that this compound was bromanil, a conclusion which was supported by the agreement between its properties and those of bromanil. In order further to test the similarity of this re-

action to that of Losanitsch, some of the yellow acid liquid, from which bromanil had been precipitated, was neutralized with calcic carbonate, when a yellow precipitate was formed. This precipitate dissolved in hydrochloric, and from this solution a white precipitate was thrown down upon addition of ammonic hydrate, the coloring-matter having been left in solution. The precipitate was insoluble in acetic acid and gave carbonic dioxide when treated with manganese dioxide and sulphuric acid. This was, therefore, calcic oxalate, and oxalic acid was a product of this reaction, as it was of the reaction of Losanitsch. The main product of Losanitsch's reaction was dibromdinitromethane, and the properties of this compound were identical with those of the yellow oil obtained in all these experiments so far as the latter were observed. No particular study was given to this compound, because of the unpleasant properties of the substance and because it had been very thoroughly studied by Losanitsch. The remaining compound obtained by Losanitsch was picric acid. At no time was any considerable quantity of picric acid obtained in these experiments, though the yellow color of all of the solutions may have been due to very small quantities of this compound. No definite proof of its formation was obtained as the yellow matter which colored the solutions was in too small quantity to yield anything definite.

Dibromdiethoxyquinone.

In order to prove that the yellow compound was bromanil, it was treated with sodic phenylate according to the directions of Jackson and Grindley. Two grams of the substance were treated with an absolute alcoholic solution of sodic phenylate prepared by acting upon absolute alcohol with 0.3 gram sodium and adding 3 grams phenol. The reaction began immediately after the phenylate came in contact with the bromanil, and the solution became deep red. To insure the completion of the reaction, the mixture was gently warmed, when the bromanil gradually disappeared and was replaced by a white precipitate. The solution was filtered, but no solid matter was obtained except the white substance which was shown to be sodic bromide. It is at this point that the first

difference between this reaction and that of Jackson and Grindley was noticed, as their organic product was not dissolved by the alcohol in which the reaction was carried on. The red alcoholic solution was diluted with water, when a red crystalline precipitate separated. This compound was made, it should be said, by using bromanil, made by the method of Stenhouse, as well as from the bromanil prepared in the reaction described above, and these observations were taken as proof that the compound assumed to be bromanil was in fact nothing else. The compound which had been precipitated with water was recrystallized from alcohol and analyzed with the following result :

0.2242 gram of the substance gave by the method of Carius 0.2363 gram of argentic bromide.

	Calculated for $C_6O_2Br_2(OC_2H_5)_2$	Found.
Br	45.19	44.86

This compound was also prepared by acting on bromanil with absolute alcohol and potassic acetate (anhydrous). This reaction yielded about 50 per cent. of the theoretical amount. The compound was also made when bromanil was boiled with sodic carbonate and absolute alcohol. This method of preparation was the most suitable for the preparation of the compound, as the yield was better than that of any other method, and the compound was essentially pure. It was also possible to prepare this substance by treating bromanil with sodic ethylate, but there was much oily matter produced, no doubt by a subsequent action of the excess of reagent on the main product in a manner similar to that observed by Jackson and Grindley in the case of dibromdiphenoxyquinone and sodic methylate. Bromanil was boiled with argentic oxide and absolute alcohol and the same compound was found as in the reactions described above, but in this case prolonged boiling was required and the yield was very small. These numerous methods of preparation as well as the analysis recorded above, show conclusively that the compound is dibromdiethoxyquinone. In this connection it is perhaps of some importance to record two negative results. Bromanil was boiled with absolute alcohol and calcic hydrate, also with ab-

solute alcohol and baric hydrate, but in neither case did any reaction take place.

Properties of Dibromdiethoxyquinone.—It crystallizes from alcohol in orange-red prisms with square ends. These prisms appear to be square and to belong to the trimetric system. The melting-point is 139°. It is freely soluble in ethyl or methyl alcohol when hot but much less soluble in cold alcohol. It is soluble in ether, glacial acetic acid, and carbonic disulphide, and very freely soluble in cold benzol, chloroform, and acetone. In water it is insoluble either cold or hot. It dissolves in concentrated nitric or sulphuric acid, but does not appear to undergo any reaction. From the hot nitric acid solution, it crystallizes on cooling. Concentrated hydrochloric acid has no action on it, but it reacts with potassic hydrate or aniline, and is by glacial acetic acid and zinc dust reduced to a colorless compound presumably the corresponding hydroquinone. None of these reactions have however been studied.

Experiments were next made to determine the modification of conditions necessary in order to produce the dibromdiphenoxyquinone instead of the diethoxy compound, and it was found that if ordinary 95 per cent. alcohol was used instead of absolute alcohol, the product did not dissolve in the alcohol used in the experiment, and when it was filtered out showed by the melting-point and other properties that it was the compound described by Jackson and Grindley, dibromdiphenoxyquinone. It should be remarked that the analysis quoted above shows by the low percentage that the analyzed sample contained a small quantity of dibromdiphenoxyquinone that could not be removed by recrystallization. The melting-point did not differ perceptibly from that of the compound prepared by different reactions where it could not contain any of the diphenoxy compound. These results make it possible to extend and slightly modify the observations of Jackson and Grindley regarding the difference of behavior of sodic phenylate towards chloranil and bromanil. They find that chloranil when treated with aqueous sodic phenylate substitutes two phenoxy groups for two chlorine atoms ; with alcoholic sodic phenylate all four chlorine atoms are replaced, two with phenoxy groups and two with ethoxy groups. Bromanil on the

other hand gives with an alcoholic solution of sodic phenylate, if a small percentage of water is present, diphenoxy derivative, while, if the sodic phenylate is dissolved in absolute alcohol instead, a diethoxy derivative results.

LX.—RESEARCHES ON THE CYCLOAMIDINES : PYRIMIDINE DERIVATIVES.

By H. L. WHEELER.

For convenience of reference, in this work, those compounds which have the amidine formation
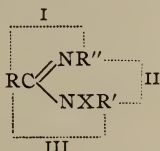
in which two of the radicals R, R', and R'' are replaced by a ring structure or a bivalent grouping, are referred to as cycloamidines. The dotted lines in the above formula show the three possible ways of replacing the radicals, and they indicate three forms of cycloamidines. It will be noticed, however, that III is the tautomeric form of I. The tautomeric form of II being obtained when the position of the hydrogen X is changed to the opposite nitrogen atom. There are therefore only two types of cycloamidines, each type having a pseudomeric or tautomeric form as in the case of the simple amidines.

The *first type*, which contains only one of the nitrogen atoms in the ring is represented by such compounds as α-aminoquinoline, the α-aminobenzoxazines, etc.

The *second type*, with both nitrogen atoms in the ring structure, is found in the anhydro bases, glyoxalines, lophin, etc.

Then, further, combinations of these types and their tautomeric forms occur : The cyanalkines, α-amino- and anilido-pyrimidines, aminoquinoxalines, cyanuramide, dicyanorthophenylenediamines, and the like, are examples of the combination types.

The object of the work, of which this paper gives a preliminary account, is primarily to investigate the action of alkyl halides on some of these cycloamidines which have not yet been examined in this respect, and also to compare this action in general with that of the simple amidines.

Pechmann[1] assumes that when a simple amidine, represented by the general formula above, is acted on with alkyl iodides, the hydrogen X is directly replaced, and hence this reaction serves to determine structure.

It seems to the writer that alkyl iodides may be added either to the amido group or to the imido group or, when the substituents are similar,[2] to both and perhaps to the atoms joined by double union. In two of the latter cases an amidine would result of a different structure from that obtained by direct substitution, so that this method of determining structure seems to be not without objection.

The cycloamidines, in general, unite with alkyl iodides and a number of cases have been described among those of the first type, where no direct substitution or replacement of hydrogen in the amino group takes place, at least not as the first step of the reaction. To illustrate this the following may be cited : Thiele and Ingle[3] obtained dialkylaminotetrazols by the action of alkyl iodides on aminotetrazol. They believe that in these only one of the alkyl groups replaces hydrogen of the amino group. Claus[4] shows that α-aminoquinoline takes up alkyl iodides in the same manner as the quinoline and pyridine bases in general, and that the amino-hydrogen is not substituted. Again, E. v. Meyer[5] has shown in several cases that the cyanalkines form similar addition-products, the amino group not being substituted.

Even acyl chlorides add to the cyanalkines without substituting the amino group. Herfeldt[6] found that cyanbenzylin or aminophenyldibenzylmiazin unites with acetyl and benzoyl

[1] Ber. d. chem. Ges., **28**, 2362 and 869.

[2] Pechmann (*loc. cit.*) found that when the substituents are similar radicals, the amidine gave two isomeric alkylated products. This is precisely what would be expected if the action is one of addition. There being in that case no decided tendency to addition entirely to either one of the nitrogen atoms.

[3] Ann. Chem. (Liebig), **287**, 249.   [4] J. prakt. Chem., **17**, 209.

[5] *Ibid.* **22**, 266, and **39**, 265.   [6] *Ibid.* [2], **53**, 249.

chlorides to form well crystallized addition-products, and that an acetyl or benzoylcyanbenzylin was not obtained. In these cases it is a tertiary nitrogen which is the point of attack or addition.

The action of alkyl iodides on the cycloamides of the second type is that of addition also, and, as in the case of the simple amidines, this action has generally been considered to be a direct replacement of hydrogen, since by treating the addition-product with alkali alkyl compounds result. The same question arises here as in the case of the simple amidines. That the alkyl group invariably replaces the hydrogen, however, has not been proved. It is not improbable that, like the cycloamidines of the first class, it is the tertiary nitrogen that unites with the alkyl halide.

The writer has found that phenylmethylanilidopyrimidine acts with methyl and ethyl iodides forming stable addition-products, and that no substitution takes place, that the alkyl iodide unites with one of the tertiary nitrogen atoms of the ring and not with the anilido group follows in all probability from the behavior of these products with alkali :

$$C_{17}H_{15}N_3.CH_3I + NaOH = C_{17}H_{15}N_3 + CH_3OH + NaI.$$
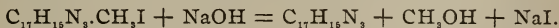
That is, methyl alcohol and sodium iodide are quantitatively formed, and unaltered anilidopyrimidine is regenerated. The formula that appears most probable for these addition-products is therefore either I or II, and from analogy a similar structure might be expected in the case of the alkyl halogen addition-products of the simple amidines.[1]

[1] The fact that the alkyl iodide addition-products of the simple amidines give up hydrogen iodide and not the alkyl group as above cannot be considered as showing that the addition takes place to the —NH— group of the amidine. To be sure, the

grouping $\diagdown N \diagup{\overset{\displaystyle H}{\underset{\displaystyle \underset{CH_3}{\diagup} \overset{\displaystyle \diagdown}{} I}{}}}$ would be expected to give up hydrogen iodide, and those

alkyl iodide addition-products of the cyloamidines which do not separate hydrogen iodide most probably do not have this grouping. But it cannot be maintained that because an addition-product gives up hydrogen iodide, it has this grouping.

$$\begin{array}{c} CH_3 \\ | \\ C \\ CH_3-N \diagdown \diagup CH \\ C_6H_5C \quad C-NHC_6H_5 \\ \diagdown N \diagup \end{array}$$

I

$$\begin{array}{c} CH_3 \\ | \\ C \\ N \diagup \diagdown CH \\ C_6H_5C \quad C-NHC_6H_5 \\ \diagdown N \diagup \\ | \\ CH_3 \ I \end{array}$$

II

$$\begin{array}{c} R \\ | \\ R''N=C-NHR' \\ \diagup \diagdown \\ CH_3 \ I \end{array}$$
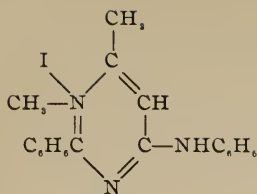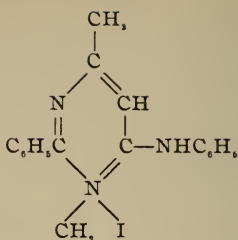
III

This being the case, the structure of the simple amidines must be completely revised, and the opposite or so-called tautomeric structure must be assigned to them. At any rate, no method has yet been devised for determining the structure of the amidines in question that is without objection.
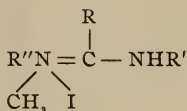
It will be shown below that phenylmethylpyrimidon, a cycloamidine of the second type, unites with one molecule of methyl iodide to form a beautiful crystalline addition-product of formula IV or V.

$$\begin{array}{c} CH_3 \\ | \\ C \\ N \diagup \diagdown CH \\ C_6H_5C \quad CO \\ \diagdown N \diagup \\ \diagup | \diagdown \\ CH_3 \ I \quad H \end{array}$$

or

$$\begin{array}{c} CH_3 \\ | \\ C \\ CH_3-N \diagdown \diagup CH \\ C_6H_5C \quad CO \\ \diagdown N \diagup \\ | \\ H \end{array}$$
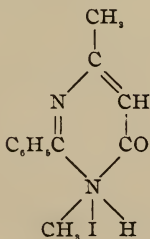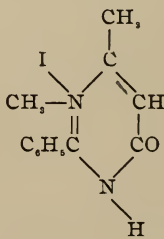
IV   V

This compound, on treatment with alkali, gives up hydrogen iodide and not the alkyl group, and an alkylated pyrimi-

don results. This alkyl derivative differs decidedly from the product obtained by heating phenylmethylchlorpyrimidine with sodium methylate. The alkyl iodide therefore is added to one of the nitrogen atoms of the pyrimidon ring, while Pinner[1] found that, if the oxypyrimidine is heated with ethyl iodide in the presence of alkali, the ethyl group attaches itself to oxygen.

In order to determine to which nitrogen the alkyl halide is added, a synthesis of the methylpyrimidon was attempted as follows: Methylbenzamidine hydrochloride was prepared. This, with acetoacetic ester, according to Pinner's explanation of the formation of the pyrimidines, might be expected to give the base corresponding to formula IV. It was found, however, that methylbenzamidine does not give a pyrimidine derivative with acetoacetic ester, at least not under the same conditions that benzamidine does, so that for the present the question of the position of the alkyl group must be left undecided.

Nef[2] has shown that carbostyril is not acted on by ethyl iodide. The above pyrimidon differs from carbostyril, in its ring structure, in having a tertiary nitrogen. It would seem most probable therefore that it is due to this that the substance takes up methyl iodide and that the addition-product is perhaps best represented by formula V.

Experimental Part.

Phenylmethylanilidopyrimidine, C_6H_5C

$$N—C.CH_3$$
$$CH$$
$$N—C—NHC_6H_5$$
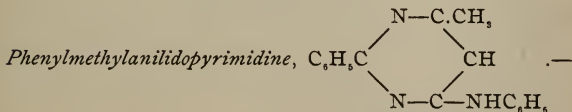
This was prepared according to Pinner's[3] directions by warming phenylmethylchlorpyrimidine with aniline. Instead of purifying the material by dissolving the reaction-product in alcohol and precipitating it with ether, it was found best to crystallize it directly from water, precipitate the base from the hot aqueous solution and then crystallize this from benzene and alcohol. The material thus obtained crystallizes in

[1] Die Imidoäther und ihre Derivate, p. 343.   [2] Ann. Chem. (Liebig), **276,** 242.
[3] Die Imidoäther und ihre Derivate, p. 248.

clusters of small prisms and melts at 160°–161°. Pinner gives its melting-point as 150°–153°.

The *hydrochloride* was obtained in colorless needles melting at 240° as described by Pinner.

The *hydrobromide* was obtained by precipitating the base from a benzene solution with hydrobromic acid gas. It forms minute needles when crystallized from alcohol and it melts at 250°.

The *hydroiodide* forms colorless needles melting at 231°.

Phenylmethylanilidopyrimidine methyl iodide.—Six grams of the above cycloamidine were heated with an excess of methyl iodide in methyl alcohol solution for seven hours from 100°–105°. The material was then washed with alcohol and crystallized from water and alcohol. Thus obtained, the substance melts at about 210°–213° with strong effervescence. If suddenly heated it melts much lower. The material dried in the air contains 2 molecules of water of crystallization. [Analysis I. and II.] When dried at a temperature of 130° it was obtained anhydrous [Analysis III.]. Determinations I. and III. were made by dissolving the substance in water and precipitating with silver nitrate. Determination II. was made by the method of Carius.

	Calculated for			Found.	
	$C_{18}H_{18}N_3I.2H_2O.$	$C_{18}H_{18}N_3I.$	I.	II.	III.
I	28.9	31.5	28.8	28.7	31.5

This addition-product is readily soluble in warm water and in alcohol, from which it crystallizes in fine, colorless needles. Ammonia or alkali immediately precipitates a substance melting at 160°–161°, which has all the properties of phenyl-methylanilidopyrimidine.

Phenylmethylmethylanilidopyrimidine,

$$C_6H_5C \underset{\displaystyle N—C—NCH_3C_6H_5}{\overset{\displaystyle N—C—CH_3}{\diagdown \diagup}} CH$$
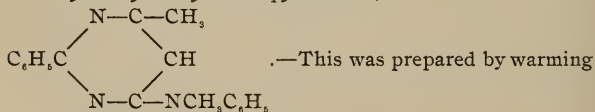
.—This was prepared by warming phenylmethylchlorpyrimidine with methyl aniline. It is the compound that should result by treating the above addition-product with alkali, if the action of methyl iodide on the

cycloamidine takes place by substitution. A comparison of
the above with the following properties show that these com-
pounds are different. This compound crystallizes from alco-
hol in colorless prisms which melt at 113°. It dissolves
readily in ether, alcohol, and benzene, but is insoluble in
water. A nitrogen determination gave :

	Calculated for $C_{18}H_{17}N_3$.	Found.
N	15.2	15.0

This compound dissolves readily in dilute hydrochloric
acid, and platinum chloride gives a bright yellow, granular
precipitate, which melts at about 228°, with effervescence.

The *hydroiodide* is readily soluble in warm alcohol, less
readily in water. It melts when slowly heated at about 198°.
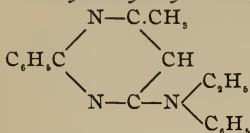An iodine determination gave :

	Calculated for $C_{18}H_{18}N_3I.2H_2O$.	Found.
I	28.9	28.9

The *nitrate* separates from dilute nitric acid in long, color-
less needles or prisms, which melt with violent effervescence
at about 170°.

Phenylmethylanilidopyrimidine ethyl iodide.—This was ob-
tained when 5 grams of phenylmethylanilidopyrimidine were
heated with 10 grams of ethyl iodide for twelve hours at 120°–
130°. The reaction-product was extracted with hot water
and then crystallized from alcohol, when it separated in color-
less needles melting at about 215°. When crystallized from
water the material shrivels at about 115°, then melts with
effervescence at or near 215°. An iodine determination of
air-dried material indicates that the substance separates with
1 molecule of water of crystallization. [Analysis I.] The
material dried at 120°–130° becomes anhydrous. [Analysis
II.]

	Calculated for		Found.	
	$C_{19}H_{20}N_3I.H_2O$.	$C_{19}H_{20}N_3I$.	I.	II.
I	29.19	30.4	29.24	30.3

This addition-product and the analogous methyl compound
give off the methyl iodides when heated to their melting-
points. Ammonia or alkali precipitate phenylmethylanilido-
pyrimidine from aqueous or alcoholic solutions.

Phenylmethylethylanilidopyrimidine,

$$\begin{array}{c} \text{N---C.CH}_3 \\ \diagup \qquad \diagdown \\ \text{C}_6\text{H}_5\text{C} \qquad \text{CH} \\ \diagdown \qquad \diagup \quad \diagup \text{C}_2\text{H}_5 \\ \text{N---C---N} \diagdown \\ \qquad \qquad \diagdown \text{C}_6\text{H}_5 \end{array}$$

.—This was prepared like the corresponding methylanilidopyrimidine for the sake of comparison with the base obtained from the above addition-product. It is an entirely different base. This melts at 87° when crystallized from alcohol. It is readily soluble in hot alcohol, difficultly in cold, and insoluble in water. It separates in beautiful, long, colorless prisms. A nitrogen determination gave :

	Calculated for $C_{19}H_{19}N_3$.	Found.
N	14.53	14.56

The *hydrochloride* is difficultly soluble in cold water, readily in hot, and crystallizes in colorless needles which appear to be hydrous. On heating the material shrivels at about 100°, then melts at about 210°.

The *platinum chloride salt* separates as a bulky, light-yellow precipitate. It is insoluble in hot water, and melts at about 218°.

The *hydroiodide* crystallizes in prisms.

An attempt to prepare an ethyl bromide addition-product of phenylmethylanilidopyrimidine was unsuccessful. 3.8 grams of anilidopyrimidine were heated with an excess of ethyl bromide from 102°–104° for five hours, when the material was found to be unaltered. It was heated again, this time with the addition of some alcohol, the temperature being kept between 120°–130° for seventeen hours. On opening the tube then, the products were found to be the hydrobromide of phenylmethylanilidopyrimidine described above, and ether. Ethyl bromide, therefore, neither effects substitution nor addition.

Phenylmethylpyrimidon methyl iodide.—Phenylmethyloxypyrimidine and methyl iodide, 4 grams of the former and 10 of the latter, were heated for six hours at 100°. No reaction was evident. The material was then heated for nine hours at

170°, when addition took place. The material dissolved almost entirely in water and, on concentrating the aqueous solution to a syrup, a mass of needles was obtained. This was crystallized from alcohol when beautiful, large, colorless prisms separated. These did not melt sharply, but decomposed with effervescence at 230°. An iodine determination gave:

	Calculated for $C_{11}H_{10}N_2O.CH_3I.$	Found.
I	38.7	38.6

n-Methylphenylmethylpyrimidon.—When the above compound with methyl iodide was dissolved in a little water and dilute alkali was added, this compound separated as a mass of colorless needles. It was purified by crystallizing from water, when it separated in the form of beautiful, large prisms, which melt at about 91°–92°. A nitrogen determination gave:

	Calculated for $C_{12}H_{12}N_2O.$	Found.
N	14.0	13.6

This compound has basic properties; it dissolves readily in dilute acids, the ordinary salts being all quite soluble. It is readily soluble in alcohol and ether, less readily in water, and is not dissolved by a small amount of alkali. The nitrate and platinum chloride double salt are the least soluble of the ordinary salts. These were obtained by spontaneous evaporation of the solutions.

The *nitrate* crystallizes in colorless, flattened prisms which melt with effervescence at about 195°.

The *platinum chloride* double salt separates in form of very large prisms with the color of azobenzene. It gave no definite melting-point below 275°, but turned dark at about 235°.

Methylbenzamidine hydrochloride, $C_6H_5C(NH)NHCH_3.HCl.$ —This was prepared by dissolving benzimidoethylester hydrochloride in a 33 per cent. solution of methylamine. On adding the hydrochloride to the solution of the amine the free ester separates; on shaking this dissolves, and in a short time a mass of colorless needles separates. This material was crystallized from water in which it is not extremely soluble. A chlorine determination gave:

	Calculated for $C_8H_{10}N_2.HCl$.	Found.
Cl	20.82	20.75

The properties of this amidine hydrochloride apparently differ decidedly from those of the corresponding ethylamidine. Lossen[1] prepared ethylamidine hydrochloride in a state of purity only with some difficulty, while Pinner[2] obtained the hydroiodide as an oil which would not crystallize.

NEW HAVEN, March, 1898.

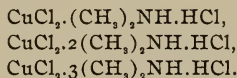
SOME DOUBLE SALTS CONTAINING SELENIUM.

BY JAMES F. NORRIS.[3]

INTRODUCTION.

A large number of double halides containing the aliphatic amines has been prepared. These show greater complexity than the double salts of ammonium or the alkali metals. Where all the possible combinations have been determined, the series of salts found are more complete, and a greater variety in composition is exhibited. For example, bismuth forms the following iodides[4] with dimethylamine:

$$2BiI_3.3(CH_3)_2NH.HI,$$
$$3BiI_3.4(CH_3)_2NH.HI,$$
$$3BiI_3.5(CH_3)_2NH.HI.$$
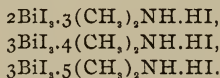
Copper has the complete series:[5]

$$CuCl_2.(CH_3)_2NH.HCl,$$
$$CuCl_2.2(CH_3)_2NH.HCl,$$
$$CuCl_2.3(CH_3)_2NH.HCl.$$

And, finally, the following double chlorides of mercury[6] have been described:

$$5HgCl_2.(CH_3)_3N.HCl,$$
$$2HgCl_2.(CH_3)_3N.HCl,$$
$$HgCl_2.(CH_3)_3N.HCl,$$
$$HgCl_2.2(CH_3)_3N.HCl.$$

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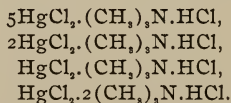
[1] Ann. Chem. (Liebig) **265**, 159.   [2] Ber. d. chem. Ges., **11**, 7.

[3] From the Author's Dissertation submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June 1895. The work was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

[4] Ann. Chem. (Liebig), **210**, 310.   [5] Jsb. d. Chem., 1883, 618.

[6] *Ibid.*, 1883, 618.

The general conclusion that the double halides containing the substituted ammonias are more complex than those containing ammonia and the alkali metals is strengthened by the results of the investigation of the selenium compounds. The influence of the introduction of alkyl groups on the stability of the halides of selenium is noticeable. Selenium tetrachloride is decomposed by water, and, even in the presence of strong hydrochloric acid, is not capable of entering into a double salt with ammonium chloride. Muthmann and Schäfer,[1] in their study of the double halides of selenium and ammonium, found that the only chloride possible was one of the composition $2SeO_2.NH_4Cl.2H_2O$, in which there is a complete breaking down of the selenium tetrachloride.

The work on the compounds containing dimethyl- and trimethylamine brings out the fact that owing to the presence of these bases, selenium can enter into combination as the oxychloride, $SeOCl_2$, where the molecule of the tetrachloride has undergone only half decomposition. The salts $SeOCl_2.(CH_3)_2N.HCl$ and $2SeOCl_2.3(CH_3)_3NH.HCl$ were obtained, when concentrated hydrochloric acid was the solvent. If the trimethylamine salt is recrystallized from dilute acid, one-half of the selenium oxychloride is changed into the oxide, and the salt $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$ is obtained.

Double salts containing selenium oxychloride are not unknown. Weber[2] prepared the following salts by mixing the oxychloride with the chlorides of the respective metals : $2SeOCl_2.SnCl_4$, $2SeOCl_2.TiCl_4$, $2SeOCl_2.SbCl_5$.

The bromides about to be described also show greater complexity than those containing ammonium. With ammonium bromide Muthmann and Schäfer succeeded in making the compound $SeBr_4.2NH_4Br$, while with both dimethyl- and trimethylamine four double bromides have been obtained.

The study of a salt containing selenium oxybromide, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, led to an interesting class of double salts containing selenium and perbromides of dimethyl- and trimethylamine. An attempt was made to replace the oxygen in the above compound by crystallizing it from a solution containing a large quantity of free bromine. The salt $SeBr_4.-$

[1] Ber. d. chem. Ges., **26**, 1008.   [2] Pogg. Ann., **125**, 325.

$(CH_3)_3N.HBr$ would thus result. This was not obtained, but a well-characterized compound, which dissolved in water with evolution of bromine. Two explanations of the action of the bromine were possible : either the selenium, in the presence of such a strong oxidizing agent, entered into combination in the hexavalent state with the formation of the salt $SeBr_6.$-$2(CH_3)_3N.HBr$, or the bromine attacked the trimethylamine hydrobromide part of the compound. If the first view were the correct one, such a salt should be possible with ammonium bromide. Accordingly, the ammonium salt was made and crystallized from a solution containing bromine. The original compound, $SeBr_4.2NH_4Br$, resulted. Trimethylamine hydrobromide was next crystallized from a solution containing free bromine. A new compound, having the formula $(CH_3)_3N.$-$HBr.Br$, was obtained, which dissolved in water with the liberation of the halogen. Analogous perhalides of other aliphatic amines have recently been described.[1]

It was the intention to study the series of salts formed by mono-, di-, and trimethylamine, and to observe in what way the increase in the number of methyl groups affected the compounds. The great wealth of material found and the difficulties encountered rendered the investigation of the di- and trimethylamine compounds alone possible. With these, interesting differences have been observed, but the series must be completed before any general conclusions can be drawn.
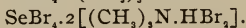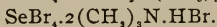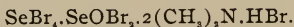
The double salts described in the following pages are tabulated below :

With Trimethylamine, $(CH_3)_3N$.

The Chlorides :

   $SeOCl_2.(CH_3)_3N.HCl$.
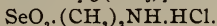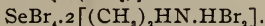 $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$.

The Bromides :

   $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$.
   $SeBr_4.2(CH_3)_3N.HBr$.
   $SeBr_4.2[(CH_3)_3N.HBr_3]$.
   $SeBr_4.1[(CH_3)_3N.HBr_3].(CH_3)_3N.HBr$.

[1] This JOURNAL, **20**, 51.

With Dimethylamine, $(CH_3)_2HN$.

The Chlorides :

$$2SeOCl_2.3(CH_3)_2HN.HCl.$$
$$SeO_2.(CH_3)_2NH.HCl.$$

The Bromides :

$$2SeBr_4.SeBr.3(CH_3)_2HN.HBr.$$
$$SeBr_4.2(CH_3)_2HN.HBr.$$
$$SeBr_4.2[(CH_3)_2HN.HBr_2].$$
$$SeBr_4.2[(CH_3)_2HN.HBr_2].(CH_3)_2HN.HBr.$$
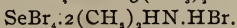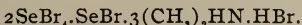
Methods of Analysis.

Selenium.—The double salts about to be described differed markedly in their action toward water. Some dissolved to a clear solution, others gave off free bromine, and still others went into solution with precipitation of selenium. The methods of analysis had to be varied, accordingly, to suit each particular case.

In the first part of the investigation, when the trimethylamine salts were studied, the selenium was determined gravimetrically. The salt was dissolved in water, sodium sulphite added, and then an excess of strong hydrochloric acid. It is necessary to have the solution acid, as an excess of sodium sulphite prevents the complete precipitation of the selenium. The solution was heated to incipient boiling until the selenium sank to the bottom of the vessel as a black powder. The precipitate was filtered into a weighed Gooch crucible and dried at 90° for two hours. This method yielded excellent results, although in most cases the amount of selenium weighed was small.

A more rapid method was desirable and, accordingly, that devised by Muthmann and Schäfer[1] was tried. As this did not give satisfactory results a new method was used, based on the reaction between sodium thiosulphate and selenium dioxide in acid solution. An account of the method has already been published.[2]

Selenium was precipitated when some of the compounds were dissolved in water. It was necessary to determine in

[1] Ber. d. chem. Ges., **26**, 1008.   [2] Norris and Fay: This JOURNAL, **18**, 703.

these cases the selenium precipitated as well as the total amount. The total selenium was determined gravimetrically as described above. That which went into solution as selenium dioxide was next determined by the volumetric method in another portion, and the precipitated selenium found by difference. This method gave better results than weighing the precipitated selenium directly, as the amount set free was usually very small.

The determination of the selenium in the compounds which gave off bromine was made gravimetrically. At first the bromine was removed by passing steam through the solution and titrating, but this method did not yield as accurate results as the gravimetric, which was accordingly used.

Halogens.—At first the gravimetric method was used for the determination of the halogens. The precipitation was made in the usual way and the precipitate filtered off while the solution was still hot, because, if allowed to cool, silver selenite crystallized out. The results came usually low when the precipitate was filtered off as soon as the solution had cleared up. It was found advisable to let the solution cool, and when the precipitate had become granular, to heat just to boiling before filtering.

The large number of analyses which had to be made rendered a quicker method desirable. The Volhard method was tested, therefore, to see if the selenium in the compounds would interfere with the accuracy of the results. When the ferric ammonium alum is added to the solution of the salt a precipitate is formed. If slightly more dilute nitric acid than is required to clear up the solution is added, the precipitation of the halogen takes place normally and the selenium compound remains dissolved. The method was tested. A weighed quantity of potassium chloride was dissolved in water containing selenium dioxide and the chlorine determined.

I. 0.1614 gram KCl gave 0.0766 gram Cl.
II. 0.2202 gram KCl gave 0.1044 gram Cl.

	Calculated for KCl.	Found. I.	II.
Cl	47.54	47.46	47.42

As stated, some of the salts gave off free bromine when dissolved in water. It was necessary to determine both the bromine set free and the total halogens in the compounds. To find the latter, the salt was weighed into a dry beaker and a dilute solution of sulphur dioxide carefully added. As the bromine was liberated it was reduced. In this solution the hydrobromic acid was determined by titration with a solution of silver nitrate. To determine the free bromine the salt was weighed into a dry glass-stoppered bottle and potassium iodide and water added. The iodine set free was that equivalent to the bromine plus that liberated by the selenium dioxide. The latter was calculated from the percentage of selenium in the compound, and the amount equivalent to the bromine found by difference. It is necessary to add a small quantity of hydrochloric acid in order to liberate the hydriodic acid, which reacts with the selenium dioxide.

The halogen in the compounds which dissolved with precipitation of selenium was determined volumetrically in the filtered solution.

<div style="text-align:center">TRIMETHYLAMINE SALTS.</div>

<div style="text-align:center">*The Chlorides.*</div>

Salt of the Composition $SeOCl_2.(CH_3)_3N.HCl$.—Selenium tetrachloride and trimethylamine hydrochloride were brought together in strong hydrochloric acid in proportions varying from three to one of the former to one to three molecules of the latter and the solution left to crystallize in a desiccator. After standing about six weeks crystals appeared, quite pure in the solutions containing an excess of selenium, but in the other beakers mixed with trimethylamine hydrochloride. The double salt was separated mechanically and proved to be the same compound which was obtained in pure condition in the solution in which the constituents had been mixed in the proportion of 2 molecules of selenium tetrachloride to one of trimethylamine hydrochloride.

The salt is exceedingly soluble in water, hydrochloric acid, and alcohol. It must be obtained by slow evaporation, for if an attempt is made to concentrate the solution by heat, a thick sirup is formed. The salt is insoluble in ether, but

dissolves in a mixture of alcohol and ether, the solubility increasing with the amount of the former. A mixture of equal parts of alcohol and ether containing concentrated hydrochloric acid is the best solvent from which to crystallize. Notwithstanding its great solubility, it can be obtained in well-defined crystals. These are colorless, monoclinic plates, elongated in the direction of the orthodiagonal axis. A careful examination was impossible, as the salt is very hygroscopic.

Two samples were analyzed with the following results :

I. 0.3154 gram salt gave 0.0946 gram Se.
II. 0.1874 gram salt gave 0.0565 gram Se.
III. 0.2263 gram salt gave 0.3693 gram AgCl.
IV. 0.1985 gram salt gave 0.3254 gram AgCl.

	Calculated for $SeOCl_2.(CH_3)_3N.HCl.$	I.	II.	III.	IV.
				Found.	
Se	30.23	30.00	30.15	....	....
Cl	40.64	....	....	40.36	40.55

Salt of the Composition $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O.$— Muthmann and Schäfer, working with the double salts containing selenium and ammonium, discovered that the only chloride possible was one of the composition $2SeO_2.NH_4Cl.$ $2H_2O$. With trimethylamine hydrochloride in strong hydrochloric acid, the decomposition of the selenium tetrachloride did not go so far, for selenium oxychloride, $SeOCl_2$, entered into combination. An attempt was accordingly made to get a salt analogous to that made by Muthmann and Schäfer. Selenium tetrachloride and trimethylamine hydrochloride were crystallized from dilute hydrochloric acid. A mixture of two salts was obtained. In order to get the second chloride in pure condition, selenium tetrachloride and trimethylamine hydrochloride, in the proportion of two molecules of the former to one of the latter, were crystallized from a mixture of equal parts of alcohol and ether. The salt was obtained in colorless, semitransparent plates. The salt described above, $SeOCl_2.(CH_3)_3N.HCl$, was converted into the same compound by recrystallization from alcohol and ether without the presence of acid. Complete breaking down of the selenium oxychloride to selenium dioxide did not take place, one-

half alone being changed. The relation between the two salts can be seen best by doubling the formula of the compound $SeOCl_2.(CH_3)_3N.HCl$.

$$SeOCl_2.SeOCl_2.2(CH_3)_3N.HCl.$$
$$SeOCl_2SeO_2 2(CH_3)_3N.HCl.H_2O.$$
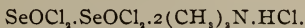
Muthmann and Schäfer found that for each molecule of selenium dioxide there was a molecule of water present in the compound. The rule is followed here also. There is but one molecule of selenium dioxide and one of water.

Another step suggested itself, the complete breaking down of the selenium oxychloride to oxide and the formation of the salt $SeO_2(CH_3)_3N.HCl.H_2O$. An attempt was made to get this salt by crystallizing selenium dioxide and the chloride of trimethylamine from alcohol and ether. Only a small amount of salt was obtained, which proved to have the composition $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$.

In making both of the chlorides, selenium dioxide and hydrochloric acid can be used instead of the chloride. The ease of preparation and the properties of the oxide render its use more advantageous.

The analyses of the two samples of the salt follow :

I. 0.2012 gram salt gave 0.0651 gram Se.

II. 0.1565 gram salt gave 0.0508 gram Se.

III. 0.2257 gram salt gave 0.2667 gram AgCl.

IV. 0.2103 gram salt gave 0.2486 gram AgCl.

	Calculated for $SeOCl_2.SeO_2 2(CH_3)N.HClH_2O.$	I.	II.	III.	IV.
			Found.		
Se	32.49	32.35	32.46	....	....
Cl	29.10	....	....	29.25	29.24

The Bromides.

A systematic search for the possible bromides was made. Selenium tetrabromide and trimethylamine hydrobromide, in varying proportions, were dissolved in hydrobromic acid and the solution evaporated to crystallization. Three different salts were formed. Special precautions were necessary to get the salts pure, as there was a great tendency for the two salts to crystallize together.

Salt of the Composition $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr.$—Two

molecules of selenium tetrabromide and one molecule of the
bromide of trimethylamine were dissolved in dilute hydro-
bromic acid, and the solution evaporated to crystallization.
On cooling, long red needles separated. These were removed,
washed with absolute alcohol, and analyzed. This salt has
attractive properties. It is stable in dry air and can be re-
crystallized from dilute hydrobromic acid, water, and alcohol.
From hot saturated solutions in acid it separates as long, stout
needles, sometimes 2 cm. in length. By slow evaporation,
large, well-developed orthorhombic crystals of a deep-red color
were obtained. The usual habit is a combination of prism,
orthopinacoid, and basal plane. At times the pyramids and
the orthodomes occur. This is the most stable of the bro-
mides containing trimethylamine and selenium, and is the form
in which the two halides tend to unite unless special precau-
tions are taken. If crystallization takes place rapidly in a so-
lution containing an excess of trimethylamine hydrobromide,
this salt crystallizes out until the solution cools, when another
compound is deposited.

There is no direct method of proving the presence of both
selenium tetrabromide and selenium oxybromide in the com-
pound, but all the facts are in accord with the formula given.
The ratio of selenium to bromine is one to four. It could not,
therefore, be a simple double halide containing selenium tet-
rabromide. And, further recognizing the tendency of the
bromide of selenium to decompose, the above formula seems
justified. As is generally admitted, the constitution of the
double halides is not expressed by any such formula as
$SeBr_4.2NH_4Br$. Accepting the explanation of their constitu-
tion advanced by Remsen,[1] in the formula given above, the
$SeOBr_2$ means simply that all of the oxygen has not been re-
placed by bromine. A constitutional formula of such a salt
can be written.

The analysis of the compound follows :

I. 0.3141 gram salt gave 0.0529 gram Se.
II. 0.3531 gram salt gave 0.0601 gram Se.
III. 0.2246 gram salt gave 0.3616 gram AgBr.
IV. 0.3281 gram salt gave 0.5277 gram AgBr.

[1] This Journal, **11**, 291.

	Calculated for $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr.$	I.	II. Found.	III.	IV.
Se	16.90	16.84	17.00	....	....
Br	68.51	....	....	68.44	68.43

Salt of the Composition $SeBr_4.2(CH_3)_3N.HBr.$—If a solution containing a large excess of trimethylamine hydrobromide in dilute hydrobromic acid is evaporated to crystallization, a dark, greenish-brown mass of fine needles mixed with the salt, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, is first deposited. If this solution is left to evaporate further in a desiccator, there appear, floating on the surface of the solution and scattered throughout the mass of green needles, large, perfectly formed, red octahedra modified by cube. These can be readily separated and the salt obtained pure. This salt proved to be the compound $SeBr_4.2(CH_3)_3N.HBr$, analogous to the ammonium, potassium, and rubidium double halides with selenium bromide. These also crystallize in octahedra. If selenium tetrabromide and trimethylamine hydrobromide, in the molecular proportions of one to two, are dissolved in dilute hydrobromic acid and the solution left to evaporate slowly, the salt is obtained generally mixed, however, with some of the green salt. It is impossible to get it from a hot, saturated solution. In this respect it differs from the potassium and ammonium salts of like composition. The analysis gave the following results :

I.   0.1589 gram salt gave 0.0183 gram Se.
II. 0.2969 gram salt gave 0.0339 gram Se.
III. 0.2718 gram salt gave 0.4501 gram AgBr.
IV. 0.1299 gram salt gave 0.2150 gram AgBr.

	Calculated for $SeBr_4.2(CH_3)_3N.HBr.$	I.	II. Found.	III.	IV.
Se	11.65	11.52	11.42	....	....
Br	70.68	....	....	70.47	70.40

A third bromide was also obtained but never in pure condition. As stated above, when a solution containing selenium tetrabromide and a large excess of trimethylamine hydrobromide was evaporated, fine greenish-brown needles were obtained, mixed with the two salts described. Renewed effort failed to discover a method of getting this salt free from the

other compounds. Under certain conditions the salt is very unstable, changing readily into the compound $SeBr_4.2(CH_3)_3$ N.HBr. If a solution containing selenium tetrabromide and trimethylamine hydrobromide, in the proportion of one molecule of the former to three of the latter, is evaporated to crystallization, the salt crystallizes out in green needles or flakes, as long as the solution is hot. If an attempt is made to remove it, the crystals break up and change to a red powder. At times the salt was obtained in good condition after the solution had cooled to the temperature of the room. The movement of the beaker was sufficient to cause a partial change from the green needles to the red powder. An analysis of this mixture showed less bromine and more selenium than was required for the salt $SeBr_4.2(CH_3)_3N.HBr$. This was evidence that the green crystals and the red powder were not two forms of the same compound. The green needles were obtained at times in a stable form, but in this case always mixed with the other two salts. When an attempt was made to recrystallize the impure green salt from hydrobromic acid, it did not go into solution at once, but sank to the bottom of the vessel as a dark brown oil, which was slowly taken up by the acid. It is hoped that further work will clear up the nature of this compound.

Salt of the Composition $SeBr_4.2[(CH_3)_3N.HBr_2]$.—This salt was first prepared as the result of the action of bromine on the compound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$. The oxy-salt was treated with bromine and concentrated hydrobromic acid and heated until solution took place. On cooling, a dark-red powder crystallized out. It was hoped in this way to replace the oxygen by bromine and to thus obtain the compound $SeBr_4.(CH_3)_3N.HBr$. The crystalline precipitate did not conduct itself, however, like a double halide of selenium and trimethylamine. It dissolved in water with evolution of bromine and, on evaporation to crystallization, the double salts above described were obtained. The study of the compound led to experiments on trimethylamine hydrobromide. This took up bromine in the same way as the double salt and was converted into the compound $(CH_3)_3N.HBr_2$. This evidently entered into combination with selenium tetrabromide

to form a double salt. The salt can be obtained best in the following manner: Selenium tetrabromide and the bromide of trimethylamine in the molecular ratio of one to two are dissolved in dilute hydrobromic acid, and the solution evaporated till, on cooling, a salt will separate out. To the hot solution is added bromine. The salt crystallizes in well-formed, stout, needle-shaped crystals of a dark-red to grayish-black color. The surface color is like that of iodine, the powder is dark-red. The salt is very stable in dry air. It can be crystallized from hydrobromic acid containing bromine, and, if the solution is allowed to evaporate slowly, the salt is obtained in large clusters of octahedra grouped together. It gives off two atoms of bromine quantitatively, when dissolved in water. The analyses resulted as follows:

I. 0.2447 gram salt gave 0.0230 gram Se.
II. 0.3545 gram salt gave 0.0336 gram Se.
III. 0.1770 gram salt gave 0.1352 gram Br.
IV. 0.2242 gram salt gave 0.1713 gram Br.
V. 0.3074 gram salt gave 0.2770 gram I.
VI. 0.1392 gram salt gave 0.1245 gram I.

In analyses V and VI the iodine is that liberated by the free bromine plus that set free by the selenium dioxide. Deducting the latter and finding the equivalent in bromine we have:

V. 0.3074 gram salt gave 0.0585 gram free Br.
VI. 0.1392 gram salt gave 0.0263 gram free Br.

	Calculated for $SeBr_4.2[(CH_3)_3N.HBr_2]$.	I.	II.	Found. III.	IV.	V.	VI.
Se	9.42	9.39	9.48	....	....	....	....
Total Br	76.28	....	....	76.37	76.44	....	....
2 atoms Br	19.07	....	....	....	....	19.03	18.90

Salt of the Composition $SeBr_4.2[(CH_3)_3N.HBr_2].(CH_3)_3N.$ HBr.—As a new kind of compound was obtained by crystallizing from solutions containing bromine, the effect of varying the proportions of the constituents was studied. In all cases, when the method described above was used, that is, crystallization from hot saturated solutions, the same compound, $SeBr_4.2[(CH_3)_3N.HBr_2]$, was obtained. But when a solution

containing a large excess of trimethylamine hydrobromide (five molecules to one of selenium tetrabromide) and bromine was allowed to crystallize slowly, a double bromide was obtained, mixed with the compound $(CH_3)_3N.HBr_2$. The salt crystallizes in red crystals, which, in general appearance, resemble the compound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$. These are easily separated from the mixture and thus obtained in pure condition. When the salt is dissolved in water, two atoms of bromine are liberated. This shows that but two molecules of the compound $(CH_3)_3N.HBr_2$ are present. The atomic ratio of selenium to bromine is one to nine. The selenium in the selenium tetrabromide requires four atoms of bromine. The two molecules of $(CH_3)_3N.HBr_2$ furnish four more. A molecule of trimethylamine hydrobromide would bring the number of halogen atoms up to nine. The analysis of the compound agrees with this composition.

I. 0.2175 gram salt gave 0.0170 gram Se.
II. 0.2260 gram salt gave 0.0379 gram Br.
III. 0.2115 gram salt gave 0.3653 AgBr..

	Calculated for $SeBr_4.2[(CH_3)_3N.HBr_2].(CH_3)_3N.HBr.$	I.	Found. II.	III.
Se	8.04	7.81	....	....
2 atoms Br	16.33	....	16.70	....
Total Br	73.50	....	....	73.49

SALTS WITH DIMETHYLAMINE.

The Chlorides.

Salt of the Composition $2SeOCl_2.3(CH_3)_2NH.HCl.$—Following the method which was used with trimethylamine hydrochloride, two double salts containing selenium and dimethylamine were obtained. The salt $2SeOCl_2.3(CH_3)_2NH.HCl$ crystallized from a solution of two molecules of selenium tetrachloride or selenium dioxide and one of dimethylamine hydrochloride in strong hydrochloric acid. The usual habit of the crystals is a combination of a monoclinic prism with the basal planes. The salt is very soluble in water, alcohol, and hydrochloric acid, and deliquesces in the air. It melts when gently heated and remains liquid for a long time. It is insol-

uble in ether. A mixture of three parts of ether and one of alcohol was used to wash the salt in preparing it for analysis. The results of the analyses follow :

I. 0.2015 gram salt gave 0.0557 gram Se.
II. 0.2082 gram salt gave 0.0578 gram Se.
III. 0.2086 gram salt gave 0.0899 gram Cl.
IV. 0.1732 gram salt gave 0.0746 gram Cl.

	Calculated for $2SeOCl_2.3(CH_3)_2NH.HCl$.	I.	II.	III.	IV.
			Found.		
Se	27.57	27.64	27.76	....	....
Cl	43.24	....	....	43.10	43.07

Salt of the Composition $SeO_2.(CH_3)_2NH.HCl$.—This salt was found when the compound $3SeOCl_2.2(CH_3)_2NH.HCl$ was recrystallized from a mixture of alcohol and ether. To obtain it directly 5 grams of selenium dioxide and 3.7 grams dimethylamine hydrochloride were dissolved in the smallest quantity of water, to which a few drops of dilute hydrochloric acid were added. The solution evaporated over sulphuric acid to a thick sirup from which, after standing two months, the salt separated in stout colorless prisms. On account of its great solubility it was difficult to free it from the adhering mother-liquor. It is interesting to note that with dimethylamine a salt containing selenium dioxide is possible, while with trimethylamine such a compound does not exist. The transition to the ammonium salt, $2SeO_2.NH_4Cl.2H_2O$, is evident. The analysis follows :

I. 0.4291 gram salt gave 0.1735 gram Se.
II. 0.4140 gram salt gave 0.3144 gram AgCl.

|	Calculated for $SeO_2(CH_3)_2NH.HCl$.	I.	II.
			Found.
Se	41.06	40.44	....
Cl	18.38	....	18.80

The Bromides.

A series of mixtures containing selenium tetrabromide and dimethylamine hydrobromide in varying proportions was made, and the resulting salts studied. The compounds differed markedly from those formed by trimethylamine. In all cases there was a considerable quantity of a salt formed which crystallized in light red needles. It was like the com-

pound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$ in color and crystal form, but, on examination, it proved to have the formula $SeBr_4.$ $2(CH_3)_3NH.HBr$. The analogous compound containing trimethylamine is obtained only under special conditions, while the salt $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$ is the form in which selenium tetrabromide and trimethylamine hydrobromide tend to unite. Mixed with the salt $SeBr_4.2(CH_3)_3NH.HBr$, in the beakers containing an excess of selenium halide, were well-formed, black crystals of a rhombohedral habit. This was the salt $2SeBr_4.SeBr.3(CH_3)_3NH.HBr$. A few green needles were formed in the solutions containing an excess of dimethylamine.

Salt of the Composition $2SeBr_4.SeBr.3(CH_3)_3NH.HBr$.—This salt can be obtained in pure condition from a solution containing a large excess of selenium tetrabromide (five molecules to one of dimethylamine hydrobromide) in strong hydrobromic acid. The solution is evaporated to such a concentration that, on cooling, the salt separates. Obtained in this way, the salt crystallizes in diamond-shaped plates of a dark-brown color. If dilute hydrobromic acid is used, a large amount of the salt $SeBr_4.2(CH_3)_3NH.HBr$ is formed. Water decomposes it with precipitation of selenium. When left exposed to the air, this decomposition takes place slowly, and the salt gradually becomes red.

In the compound of selenium and trimethylamine which contains the largest percentage of selenium, $SeBr_4.SeOBr_2.$ $2(CH_3)_3N.HBr$, the ratio of selenium to bromine is one to four. The same ratio exists in the dimethylamine salt containing the largest amount of selenium. But the fact that it is decomposed by water with the liberation of selenium, points to a different composition from that assigned to the trimethylamine salt. Some compound of selenium containing less bromine than the tetrabromide must be present, in order to have the ratio one of selenium to four of bromine. The compound Se_2Br_2 is known and, considering the instability of the tetrabromide, there is a possibility of the formation of the lower halide, and of its entering into combination to form a double salt. Further, the monobromide is decomposed by water, and selenium is precipitated and, as stated, the salt described acts in

this way. The analyses for total selenium and for bromine point to the formula given to the salt. The determination of the selenium precipitated is further evidence of its correctness. When water acts on selenium monobromide the following reaction takes place:

$$2Se_2Br_2 + 2H_2O = 3Se + SeO_2 + 4HBr.$$
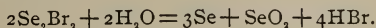
That is, three-fourths of the selenium is precipitated. Now, if $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$ is the correct formula for the salt under discussion (selenium monobromide is written SeBr for simplicity) then three-fourths of the selenium in the monobromide should be precipitated; that is, three-fourths of one-third or one-fourth of the total selenium. The analyses show that this is the case. The following results were obtained:

I. 0.2310 gram salt gave 0.0412 gram Se.

II. 0.4102 gram salt gave 0.0724 gram Se.

III. 0.2547 gram salt gave 0.0336 gram Se as SeO_2 in solution.

IV. 0.3688 gram salt gave 0.0487 gram Se as SeO_2 in solution.

V. 0.1995 gram salt gave 0.1443 gram Br.

VI. 0.2321 gram salt gave 0.1671 gram Br.

Analyses III. and IV. were of the selenium dioxide in solution. The difference between this selenium and the total amount gives that which was precipitated.

	Calculated for $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$	I.	II.	III.	IV.	V.	VI.
Total Se	17.75	17.84	17.65	...	...	....	....
Precip'd Se	4.44	....	....	4.54	4.53	....	....
Br	71.91	....	....	...	...	71.83	71.99

Salt of the Composition $SeBr_4.2(CH_3)_2NH.HBr$.— This is the form in which the two halides tend to unite. The salt is obtained in pure condition by evaporating a mixture of one molecule of selenium bromide and two of dimethylamine hydrobromide in dilute hydrobromic acid. When this takes place slowly, bright red, prismatic needles are obtained, which are comparatively stable in the air. It is very remarkable that this salt crystallizes in a different system from all the other selenium compounds of analogous composition. The double

bromides of selenium of the general formula $SeBr_4.2MBr$, namely those containing potassium, rubidium, ammonium, and trimethylamine, all crystallize in octahedra, while the dimethylamine compound crystallizes in monoclinic or triclinic prisms.

The salt was analyzed with the following results:

I. 0.2873 gram salt gave 0.0347 gram Se.
II. 0.2353 gram salt gave 0.0285 gram Se.
III. 0.3544 gram salt gave 0.6136 gram AgBr.
IV. 0.1496 gram salt gave 0.1102 gram Br.

	Calculated for $SeBr_4.2(CH_3)_2NH.HBr$.	I.	II.	III.	IV.
Se	12.13	12.07	12.11	....	....
Br	73.73	....	....	73.67	73.66

A third bromide was formed, crystallizing in bright green needles like the trimethylamine compound, which could not be obtained in pure condition. It was obtained once in considerable quantity in beautiful crystals mixed with some fine, red needles. It was impossible to separate the two compounds mechanically, so a few drops of water were added to the beaker and the salt redissolved, with the intention of removing the green salt, as soon as it was formed. When the solution cooled, only the red salt appeared. The crystals were redissolved over and over again without removing them from the mother-liquor. When the crystallization took place the results varied without any apparent rule. At times a mixture of the red and green salts was obtained, at times the pure red, but never the green alone. Finally the exact conditions were discovered, and the salt was obtained in an apparent state of purity. It can be prepared as follows: One molecule of selenium dioxide, or tetrabromide, and six of dimethylamine hydrobromide are dissolved in concentrated hydrobromic acid, and the solution evaporated at a temperature just below the boiling-point, until a salt begins to separate out on the surface of the liquid. The beaker is now set in a warm place, and left undisturbed till the solution has cooled to 60° or 70°. A large mass of fine green needles with a metallic lustre will be found. These are removed to a porous

plate and thus freed from the excess of acid. It is impossible to wash the compound, as it is readily decomposed with precipitation of selenium. If the crystals are not removed while the liquid is at the temperature mentioned, they will be contaminated by another salt, which appears as soon as the solution has cooled to the temperature of the room.

Analyses of samples of the salt prepared in this way gave results which agreed with one another, but not with any possible formula.

Salt of the Composition $SeBr_4.2[(CH_3)_2NH.HBr_2]$.—The salt was obtained in the same way as the analogous trimethylamine compound. It crystallizes in dark-red needles and is best obtained from a hot saturated solution. Its appearance and properties are like those of the corresponding salt containing trimethylamine. The following analyses were made:

I. 0.1953 gram salt gave 0.1541 gram Br.
II. 0.1847 gram salt gave 0.1453 gram Br.
III. 0.2552 gram salt gave 0.0498 gram free Br.
IV. 0.2374 gram salt gave 0.0469 gram free Br.
V. 0.3196 gram salt gave 0.0314 gram Se.
VI. 0.2044 gram salt gave 0.0200 gram Se.

	Calculated for $SeBr_4.2[(CH_3)_2NH.HBr_2]$.	I.	II.	III.	IV.	V.	VI.
				Found.		
Total Br	78.95	78.90	78.67	....	....	....	....
2 atoms Br	19.74	....	....	19.52	19.78	....	....
Se	9.74	....	....	....	....	9.88	9.78

Salt of the Composition $SeBr_4.2[(CH_3)_2NH.HBr_2].(CH_3)_2NH.HBr$.—A salt of this formula was obtained from a solution of one molecule of selenium tetrabromide and six of dimethylamine hydrobromide in strong hydrobromic acid. The solution was evaporated until a salt appeared on the surface of the liquid. Bromine was then added. On cooling, long prismatic crystals of a deep maroon color were deposited. The salt has a strong crystallizing force; the prismatic faces are well developed and possess a high lustre. It is perfectly analogous in composition to the trimethylamine salt, although quite different in appearance. It will be remembered that the compounds $SeBr_4.2(CH_3)_3N.HBr$ and $SeBr_4.2[(CH_3)_3N.$

HBr_2].$(CH_3)_3N$.HBr are obtained only by spontaneous evaporation. The dimethylamine salts of similar composition are formed with ease in hot solutions. They also crystallize in entirely different forms in different crystalline systems.

The salt gave the following figures when analyzed :

I. 0.4419 gram salt gave 0.0367 gram Se.

II. 0.3143 gram salt gave 0.0258 gram Se.

III. 0.3077 gram salt gave 0.0519 gram free Br.

IV. 0.3075 gram salt gave 0.0517 gram free Br.

V. 0.1972 gram salt gave 0.1524 gram Br.

VI. 0.2679 gram salt gave 0.2070 gram Br.

	Calculated for $SeBr_4.2[(CH_3)_2NH.HBr_2](CH_3)_2NH.HBr.$	I.	II.	III.	IV.	V.	VI.
				Found.			
Se	8.42	8.31	8.20	....	....	....	....
2 atoms Br	17.07	....	....	16.86	16.82	....	....
Total Br	76.86	....	....	....	....	77.23	77.26

Note.—Throughout the investigation the double salts were made by using selenium tetrachloride and tetrabromide, as the available supply of selenium was in these forms. It was found that selenium dioxide dissolved in the halogen acids served the purpose just as well. The oxide was made by treating selenium with concentrated nitric acid, evaporating to dryness, and subliming the residue.

Conclusion.

The double salts which have been described exhibit such complexity of structure that they cannot be rightly grouped under the class of double halides, nevertheless it is interesting to note that with one exception the number of molecules of basic halide is never in excess of the number of halogen atoms combined with the selenium. The salts thus obey Professor Remsen's law[1] and can be explained by assuming the presence of a bivalent halogen group —(Cl = Cl)—. The one exception mentioned is the compound $SeO_2.(CH_3)_2NH.HCl$. This is not a double halide at all, and, therefore, is excluded from the generalization.

[1] This JOURNAL, 11, 291.

I.—ON PHENYLGLUTARIC ACID AND ITS DERIVATIVES.

By S. Avery and Rosa Bouton.

The alkyl succinic and glutaric acids have of late been a favorite subject with investigators. During the past few years Auwers, Perkin, and others have increased our knowledge of these compounds to a marked degree. At the same time the corresponding aromatic compounds have been but slightly investigated. We have accordingly entered upon the study of these acids, hoping to widen our knowledge of the subject in general, and especially to determine the influence of the phenyl group on melting-points and the formation of anhydrides.

In the course of his investigation on the addition of sodium acetoacetic ether and of sodium malonic ether to unsaturated ethers, Michael obtained by the action of sodium malonic ether on cinnamic ether an addition-product of the formula,

$$C_6H_5CH \begin{cases} CHNaCOOR \\ \\ CH(COOR)_2 \end{cases}.$$
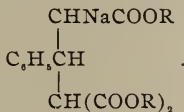
When this compound is saponified and heated it yields β-phenylglutaric acid,

$$C_6H_5CH \begin{cases} CH_2COOH \\ \\ CH_2COOH \end{cases}.$$
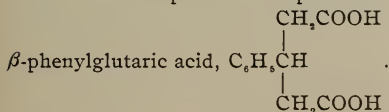
The following description is given: "Schräg[1] abgestumpfte Prismen aus Benzol, Schmelzp. 137°.5–138°.5. Unlöslich in Wasser, wenig löslich in Benzol, leicht in Alkohol und Essigäther." The results of our investigations show that Professor Michael did not obtain the acid in a perfectly pure condition. He did not investigate it further than to make and analyze a silver salt, as he very kindly informed us in a private communication. As a preliminary experiment, car-

[1] J. prakt. Chem. [2], **35**, 352.

ried out according to his method, failed to give a satisfactory yield, we endeavored to find a better method.

<div align="center">EXPERIMENTAL PART.</div>

The Action of Benzal Chloride on Sodium Malonic Ether.

Pure benzal chloride was added to sodium malonic ether in alcoholic solution (2 molecules) in the hope of obtaining benzaldimalonic ether according to the equation,

$$C_6H_5CHCl_2 + 2NaCH(COOR)_2 = C_6H_5CH \begin{matrix} CH(COOR)_2 \\ | \\ \\ | \\ CH(COOR)_2 \end{matrix} + 2NaCl.$$
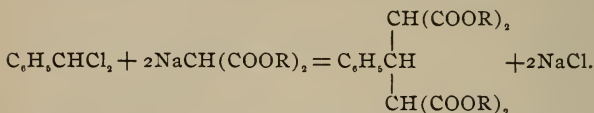
Benzaldimalonic ether would readily yield β-phenylglutaric acid by saponification and loss of carbonic anhydride. The expected reaction, however, did not take place. On distilling in a vacuum the products of the reaction, about half of the distillate proved to be malonic ether. The rest of the distillate boiled at about 250°, at a pressure of 50 mm., and proved to be benzalmalonic ether. Evidently the reaction is to be expressed by the following :

$$C_6H_5CHCl_2 + 2NaCH(COOR)_2 = C_6H_5CH=C(COOR)_2 + CH_2(COOR)_2 + 2NaCl.$$
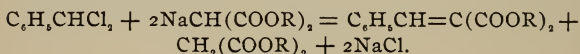
It is of interest to note in this connection that, while Guthzeit and Dressel[1] obtained methylenedimalonic ether by the action of methylene iodide on sodium malonic ether, and Perkin[2] obtained similar results, using methylene chloride, Auwers[3] was unable to obtain an analogous product when working with chloracetol.

Condensation of Benzalmalonic Ether with Sodium Malonic Ether. Formation of Benzaldimalonic Ether.

A quantity of benzalmalonic ether was made according to the method of Classen and Crismer[4] by condensing benzaldehyde with malonic ether. Equivalent quantities of benzalmalonic ether and sodium malonic ether were brought together in alcoholic solution. The mixture became hot and

[1] Ann. Chem. (Liebig), **256**, 174.   [2] J. Chem. Soc. (London), **59**, 992.
[3] Ber. d. chem. Ges., **28**, 1130.   [4] Ann. Chem. (Liebig), **218**, 132.

changed to a gelatinous mass which, on treating with dilute sulphuric acid, gave a heavy oil. This oil decomposed considerably on distilling in vacuum, hence benzaldimalonic ether could not be obtained in a pure condition. That the oil just described consists principally of this ether follows from the fact that it gives an excellent yield of β-phenylglutaric acid.

Saponification of Benzaldimalonic Ether. Formation of β-Phenylglutaric Acid.

The oil just described was saponified with a solution of barium hydrate. On acidifying, an oily mass was obtained. This product, when heated above its melting-point, evolved carbonic anhydride, but gave no crystalline product. Similar results were obtained when alcoholic potash was used for saponifying. When the oil was saponified by boiling with sulphuric acid diluted with 2 volumes of water, a resinous mass was formed, but on pouring off the hot liquid and cooling, crystals were deposited. Protracted boiling with hydrochloric acid failed to effect complete saponification; hence we tried the action of hydrobromic acid. The oil was mixed with ten times its volume of strong hydrobromic acid and heated in a flask with return-condenser for twenty-four hours. Carbonic anhydride and ethyl bromide were evolved. The solution was now evaporated to dryness on the water-bath. The residue was extracted with boiling water. On concentrating the aqueous solution a white crystalline product was obtained which, after 2 or 3 crystallizations from hot dilute hydrochloric acid, melted sharply at 140°. It formed glistening plates soluble in water, alcohol, ether, and chloroform; scarcely soluble in benzene; insoluble in petroleum ether. A combustion gave the following:

	Calculated for $C_{11}H_{12}O_4$.	Found.
C	63.46	63.22
H	5.77	6.05

It will be noticed that the properties just given do not entirely agree with the properties of Michael's acid. The compounds are, however, identical, as we obtained the same substance by treating sodium malonic ether with cinnamic ether.

The difficulties in preparing it by the latter method disappear when the condensation-product without previous distillation is saponified with hydrobromic acid. In this way we prepared a quantity of the pure acid, obtaining seventy per cent. of the amount that quantitative reactions should afford, calculated from the ethers used in the preparation.

Salts of β-Phenylglutaric Acid.

Silver salt.—Made by neutralizing the acid with ammonia and precipitating with silver nitrate. Slightly soluble in hot water.

0.2651 gram of the substance gave 0.1350 gram metallic silver.

	Calculated for $C_{11}H_{10}O_4Ag_2$.	Found.
Ag	51.16	50.93

Barium salt.—Made by neutralizing a solution of the acid with barium hydrate. Precipitated out of the aqueous solution by alcohol. Glistening, white precipitate. Easily soluble in water. The salt was dried for analysis by heating on a water-bath.

0.1104 gram salt gave 0.0686 gram $BaSO_4$.

	Calculated for $C_{11}H_{10}O_4Ba.2H_2O$.	Found.
Ba	36.14	36.36

Copper salt.—Made by neutralizing the acid with freshly precipitated copper oxide. Green crystalline precipitate; scarcely soluble in water.

0.0884 gram salt dried on a water-bath gave 0.0185 gram metallic copper.

	Calculated for $C_{11}H_{10}O_4Cu.2H_2O$.	Found.
Cu	20.76	20.927

The barium and copper salts give off water, when heated to a higher temperature, before decomposition sets in.

The lead salt resembles the silver salt. The sodium, potassium, and ammonium salts are very easily soluble in water.

β-*Phenylglutaric Anhydride.*

This anhydride is made by heating the acid above its melting-point, or by treating the acid with acetyl chloride. The latter method gives the better yield. Excess of acetyl chloride is evaporated off on the water-bath. The residue is washed with petroleum ether and dissolved in hot benzene. Petroleum ether is now added till the solution begins to be cloudy. On cooling, the anhydride separates out in the form of glistening white plates; melting-point 105°; soluble in benzene, chloroform, and ether; insoluble in petroleum ether; scarcely affected by cold water; slowly converted into the acid by boiling; instantly changed by alkalies to salts of the acid.

0.2605 gram gave 0.6639 gram CO_2, and 0.1248 gram H_4O.

	Calculated for $C_{11}H_{10}O_3$.	Found.
C	69.47	69.50
H	5.26	5.32

β-*Phenylglutaranilic acid.*—The anhydride just described reacts almost quantitatively with aniline in benzene solution forming the anilic acid. Recrystallized out of dilute alcohol, the anilic acid melts at 168°. A silver salt of this acid was analyzed.

0.1842 gram of the salt gave 0.0508 gram silver.

	Calculated for $C_{17}H_{15}O_3NAg$.	Found.
Ag	27.67	27.57

β-*Phenylglutaranil.*—This anil is readily made by heating the anilic acid in a test-tube over the open flame. Crystallized from alcohol, it forms glistening white needles, which melt at 223°.

β-*Phenylglutar-p-tolilic acid.*—This acid was made by the action of β-phenylglutaric anhydride on *p*-toluidine; melting-point 154°–155°.

0.2312 gram acid gave 9.7 cc. nitrogen. ¦T = 20°.1. Bar.= 739 mm.

	Calculated for $C_{18}H_{19}O_3N$.	Found.
N	4.71	4.66

Silver salt.—

0.2165 gram salt gave 0.0575 gram silver.

	Calculated for $C_{18}H_{16}O_3NAg$.	Found.
Ag	26.67	26.55

Comparison of the Melting-points of β-Phenylglutaric Acid and Its Derivatives with those of the Corresponding Benzylsuccinic Acid and Its Derivatives.

We made the benzylsuccinic acid by the method of Bischoff and Mintz.[1] The anhydride and its derivatives with aromatic bases were prepared by methods previously given in this paper. The results are shown in the following table:

β-Phenylglutaric acid,	140°
β-Phenylglutaric anhydride,	105°
β-Phenylglutaranilic acid,	167°–168°
β-Phenylglutaranil,	223°
β-Phenyl-*p*-tolilic acid,	154°–155°
Benzylsuccinic acid,	161°
Benzylsuccinic anhydride,	99°
Benzylsuccinanilic acid,	157°–159°
Benzylsuccinanil,	indistinct
Benzylsuccin-*p*-tolilic acid,	165°

Action of β-Phenylglutaric Anhydride on Phenol in the Presence of Sulphuric Acid.

The anhydride, when heated with phenol and sulphuric acid, gives a brownish coloration. This sulphuric acid solution, when diluted with a large excess of water, is nearly colorless. On adding an alkali a blue-green coloration is produced. The color disappears on the addition of an acid. The coloring-matter has not been isolated.

Action of Fuming Sulphuric Acid on β-Phenylglutaric Anhydride.

A few grams of the anhydride were dissolved in fuming sulphuric acid. After heating for a few minutes on the water-bath the solution was poured into ice-water. In this way a beautiful crystalline product was obtained that melted

[1] Ber. d. chem. Ges., **23**, 653.

at 153°. The crystals contained no sulphur. The amount of material was too small to permit of further investigation than the making and analyzing of a silver salt.

0.1736 gram salt gave 0.0632 gram silver.

	Calculated for $C_{22}H_{18}O_4Ag_2$.	Found.
Ag	36.33	36.40

If we assume that 2 molecules of the anhydride condense in the manner indicated by the following equation,

$$2C_6H_5CH \begin{array}{c} CH_2CO \\ | \\ \diagdown \\ | \\ CH_2CO \end{array} O = C_6H_5CH \begin{array}{c} CH_2C \\ | \\ \diagdown \\ | \\ CH_2CO \end{array} O \begin{array}{c} C COOH \\ | \\ C_6H_5CH \\ | \\ CH_2COOH \end{array},$$

we arrive at the formula of an acid whose silver salt would correspond in composition to the silver salt above given.

The Action of β-Iodopropionic Ether on Sodium Phenylmalonic Ether.

We heated these substances in alcoholic solution supposing that they would react in the following manner:

$$C_6H_5NaC(COOR)_2 + ICH_2.CH_2.COOR = \begin{array}{c} C_6H_5C(COOR)_2 \\ | \\ CH \\ | \\ CH_2-COOR \end{array} + NaI.$$

A tricarboxylic ether of this structure would in all probability readily yield the unknown α-phenylglutaric acid. We found, however, that the ethers react as follows:

$$C_6H_5NaC(COOR)_2 + ICH_2CH_2COOR = C_6H_5CH(COOR)_2 + CH_2=CH-COOR + NaI.$$

We hope to prepare α-phenylglutaric acid by another method.

II.—ON α-METHYL-β-PHENYLGLUTARIC ACID.

By S. Avery and Mary L. Fossler.

In preparing this acid we met with unexpected difficulties. Sodium methylmalonic ether and cinnamic ether were heated in alcoholic solution in the usual way. On saponifying with hydrobromic acid an oily substance was obtained. We did not succeed in obtaining a crystalline product. We next heated sodium malonic ether with cinnamic ether, neutralized with hydrochloric acid, then washed and dried the oil carefully. As one of us and Miss Bouton[1] have shown in the previous paper, this oil consists principally of phenylpropanetricarboxylic ether. This product was treated with sodium alcoholate and methyl iodide. The expected reaction was as follows :

$$
\begin{array}{ccc}
CH_2COOR & & CH_2COOR \\
| & & | \\
C_6H_5—CH & + CH_3I = C_6H_5—CH & + NaI. \\
| & & | \\
CNa(COOR)_2 & & C(COOR)_2 \\
& & | \\
& & CH_3
\end{array}
$$
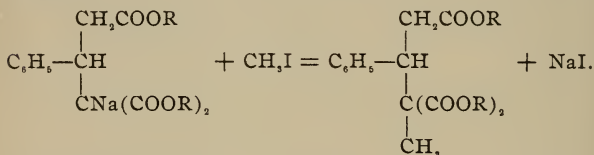
All attempts to obtain a crystalline product by saponification and heating resulted in failure. After a number of unsuccessful attempts, we finally succeeded in preparing a small quantity of α-methyl-β-phenylglutaric acid by the following method : α-Methylcinnamic acid was prepared by Perkin's[2] method and converted into the methyl ether. This was condensed with sodium malonic ether. When acidified the condensation-product yielded methylphenylpropanetricarboxylic ether, and, on saponification with caustic potash, the corresponding acid. Neither of these compounds was isolated in pure condition. The impure acid was distilled over an open flame, carbonic anhydride, water, and an oil passing off. This oil, presumably an impure anhydride of α-methyl-β-phenylglutaric acid, dissolved for the most part in ammonia.
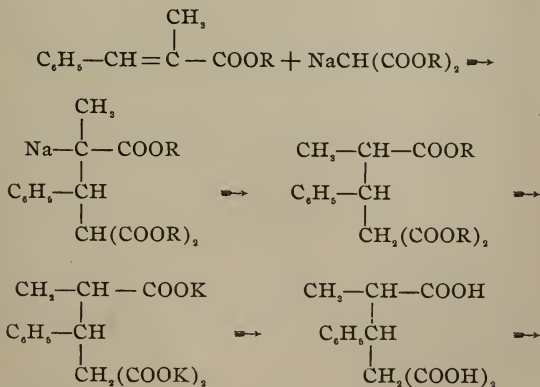
To the solution of the ammonium salt copper sulphate was added, when a green precipitate was formed. This was washed with water, alcohol, and ether; then suspended in water and decomposed with hydrogen sulphide. On evaporating the aqueous solution, crystals separated out. These were repeatedly recrystallized from benzene till the melting-point remained constant at 122°. They formed flaky, white plates; soluble in alcohol, ether, chloroform, and hot benzene; insoluble in petroleum ether. The greater part of the small quantity that remained after the repeated crystallizations was used in making a silver salt.

0.1122 gram of salt gave 0.0555 gram silver.

	Calculated for $C_{12}H_{12}O_4Ag_2$.	Found.
Ag	49.46	49.46

On treating the acid with acetyl chloride a substance resembling an anhydride was formed. The amount of material did not permit of our obtaining the anhydride in a pure condition.

The reactions by which the acid was prepared may be indicated as follows:

$$C_6H_5-CH=\overset{\overset{\textstyle CH_3}{|}}{C}-COOR + NaCH(COOR)_2 \longrightarrow$$

$$\underset{\underset{\textstyle CH(COOR)_2}{|}}{\overset{\overset{\textstyle CH_3}{|}}{\underset{C_6H_5-CH}{Na-C-COOR}}} \longrightarrow \underset{\underset{\textstyle CH_2(COOR)_2}{|}}{\overset{\overset{\textstyle CH_3-CH-COOR}{}}{C_6H_5-CH}} \longrightarrow$$

$$\underset{\underset{\textstyle CH_2(COOK)_2}{|}}{\overset{\overset{\textstyle CH_3-CH-COOK}{}}{C_6H_5-CH}} \longrightarrow \underset{\underset{\textstyle CH_2(COOH)_2}{|}}{\overset{\overset{\textstyle CH_3-CH-COOH}{}}{C_6H_5CH}} \longrightarrow$$

$$
\begin{array}{ccc}
\underset{|}{CH_3}-CH-CO & & CH_3-\underset{|}{CH}-COONH_4 \\
C_6H_5-\underset{|}{CH} \qquad O \;\rightarrow\; & & C_6H_5-\underset{|}{CH} \qquad\qquad \rightarrow \\
CH_2-CO & & CH_2COONH_4
\end{array}
$$

$$
\begin{array}{ccc}
\underset{|}{CH_3}-CHCOO & & CH_3-\underset{|}{CH}-COOH \\
C_6H_5-\underset{|}{CH} \qquad Cu \;\rightarrow\; & & C_6H_5-\underset{|}{CH} \qquad\qquad . \\
CH_2COO & & CH_2COOH
\end{array}
$$
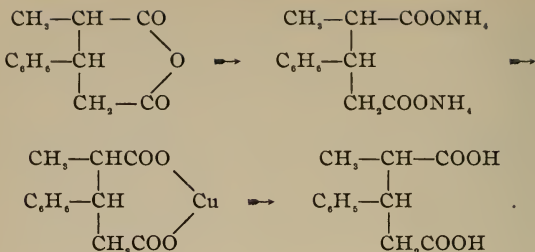
We lost the greater part of the acid on recrystallizing. A glance at the formula will show the presence of two asymmetric carbon atoms. The oily condition of the acid and the difficulty in purifying probably arose from the presence of stereoisomers.

We shall investigate this subject further as well as the isomers and homologues of the compounds described.

REVIEWS.

Methods for the Analysis of Ores, Pig Iron, and Steel in Use at the Laboratories of Iron and Steel Works in the Region about Pittsburg, Pa. Together with an Appendix containing various special methods of analysis of ores and furnace products. Contributed by the chemists in charge, and edited by a Committee of the Chemical Section, Engineers' Society of Western Pennsylvania. Chemical Publishing Co., Easton, Pa. 1898. iv + 133 pp. Price $1.00.

In the circular first sent out by the committee a request was made that the chemists addressed shall furnish a full description of the methods used in the daily laboratory work for the determination of the following substances :

In Ores—Silica, iron, phosphorus, manganese.

In Pig Iron—Silicon, sulphur, phosphorus, manganese.

In Steel—Carbon (by combustion), sulphur, phosphorus, manganese, nickel.

The report gives the methods in use in 16 different laboratories. The report was at first published by the Engineers' Society of Western Pennsylvania, but the edition having been exhausted it is republished in a more convenient and more generally accessible form.

The exigencies of the iron and steel laboratories, which require an enormous number of analytical determinations, have

caused the development of many rapid methods, some of which are at the same time very accurate. The present work, from its nature, gives a compilation of those methods which have stood the test of actual use and of the comparisons which come with fierce business competition. The value of such a book is evident. The descriptions of methods are, of course, concise, and repetition is avoided by constant reference to published methods, especially to those in Blair's Analysis of Iron, but those engaged in this field of work will find in the study of the book very many useful suggestions.

<div align="right">W. A. N.</div>

THE CALORIFIC POWER OF FUELS. Founded on Scheurer-Kestner's Pouvoir Calorifique des Combustibles, with the addition of a very full collection of tables of heats of combustion of fuels, solid, liquid, and gaseous, to which is also appended the report of the Committee on Boiler Tests of the AMERICAN SOCIETY OF MECHANICAL ENGINEERS (December, 1897); tables of constants used. By HENRY POOLE, F.C.S., member of the Society of Chemical Industry; the American Chemical Society; the American Society of Civil Engineers; the American Society of Mechanical Engineers; etc. First edition. First thousand. 8vo. Cloth. 40 figures, 279 pages. $3.00. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1898.

After discussing units, definitions, and thermometers, the various formulæ for calculation of the calorific power from the chemical composition are treated in detail. The statement that these formulæ are more applicable to cokes and hard coals rather than to bituminous, would seem to be open to question. The Berthier (litharge) test is not given the credit to which it is entitled.

The next 3 chapters deal with the principal calorimeters, that of Mahler and its method of working being described sufficiently minutely to be used in the laboratory; the discussion of the errors and corrections is especially full. The chapters upon the three kinds of fuel would hardly appear to be ''adapted to American methods and data,'' as with few exceptions, the analyses and tests are those obtained in European practice.

The remaining chapters are devoted to the determination of the calorific power of fuel burned under a steam boiler; these are clearly written and unusually complete. The methods of sampling gases described are too expensive and troublesome to find universal adoption.

In addition to the report indicated on the title-page, the appendix contains many useful tables. Especially noteworthy are those giving the analysis and calorific power of fuels from all parts of the world.

The work will be of value to everyone interested in the application of fuel. Its value would have been increased to the

investigator had it contained more references to the original sources.   A. H. GILL.

THE TUTORIAL CHEMISTRY. Part I, Non-metals; Part II, Metals. By
G. H. BAILEY, D.Sc., London, Ph.D., Heidelberg, Lecturer in
Chemistry in the Victoria University. Edited by WILLIAM BRIGGS,
M.A., F.C.S., F.R.A.S., Principal of University Correspondence Col-
lege. London : W. B. Clive, University Correspondence College
Press. Hinds & Noble, 4 Cooper Institute, New York.

The London University Correspondence College is an asso-
ciation of teachers who fit students by correspondence for the
London University examinations.   We might think that in-
struction given in this way would be superficial or mere
cramming.   An examination of these two volumes shows that
Dr. Bailey, whose research work is favorably known to all
chemists, has given an admirable condensed presentation of
the facts and theories of inorganic chemistry, and shows
furthermore that systematic laboratory work and a great deal
of it is demanded.

In the first volume, on non-metals, all experiments are de-
scribed in the text and each chapter closes with questions for
self-examination ; the last chapter treats of chemical calcula-
tions with examples and problems.

The treatment of the second volume, on metals, is original ;
the first 100 pages are given to physical chemistry under the
following heads : Determination of atomic weight, relations
between the atomic weights, constitution of gaseous com-
pounds, constitution of liquid compounds, solution.   The
author admits in the preface that this section ''may ap-
pear somewhat difficult to a chemist in his second year
of study,'' but he believes that no real obstacle will be
met, provided the student has already had some experience
in dealing with physical problems.   A perusal of this part
of the book leads the reviewer to share this belief, as Dr.
Bailey's presentation of the subject is very clear and as simple
as possible.   The remaining 200 pages are given to the chem-
istry of the metals, directions for experiment being relegated
to the appendix, which also includes a few pages on crystal-
lography and spectrum analysis.

Dr. Bailey's work is cordially recommended to those who
wish a concise text-book of inorganic chemistry, thoroughly
up to date in matter and treatment, but the chapters on phys-
ical chemistry would be valueless to many American college
students of chemistry, as some knowledge of physics is essen-
tial to its study.   E. R.

AMERICAN

CHEMICAL JOURNAL

A REDUCTION OF PERMANGANIC ACID BY MAN-
GANESE PEROXIDE.

By H. N. Morse and C. L. Reese.

In a previous article[1] one of us, together with Messrs. Hop-
kins and Walker, described certain experiments on the reduc-
tion of permanganic acid by precipitated manganese peroxide.
It was there concluded that, whenever the latter is introduced
into, or is formed in the presence of, the former or its salts, a
reduction of the acid occurs with an evolution of three-fifths
of its active oxygen, in accordance with the following equa-
tion :

$$x\mathrm{MnO_2} + 2\mathrm{HMnO_4} = (x + 2)\mathrm{MnO_2} + \mathrm{H_2O} + 3\mathrm{O}.$$
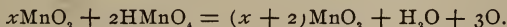
It was also shown that to this cause is to be ascribed the ob-
served instability of solutions of permanganate.

Six months later[2] there appeared an article by Messrs.
V. Meyer and Max Von Recklinghausen in which is described
the evolution of oxygen which takes place when hydrogen or
carbon monoxide is absorbed by a nearly saturated (5 per
cent.) acidified solution of potassium permanganate. The
opinion was then expressed by one of us[3] that the phenome-
non observed by Messrs. Meyer and Von Recklinghausen was

[1] This Journal, 18, 401.   [2] Ber. d. chem. Ges., 29, 2549.
[3] Ibid., 30, 48.

due to the peroxide which is formed when reducing gases are
absorbed by permanganic acid ; in other words, that it is an
instance of a kind of reaction which had been under observa-
tion in this laboratory for several years.

After the communication referred to had left the hands of
the author, but before it appeared in printed form, an article
by Messrs. H. Hirtz and V. Meyer was published[1] in which
they maintain that the phenomenon observed by Messrs.
Meyer and Von Recklinghausen is fundamentally different
from that described by Morse, Hopkins, and Walker. The
grounds for this opinion appear to be twofold. In the first
place the authors make the wholly unwarranted assumption
that Morse, Hopkins, and Walker experimented with *neutral*
solutions only, that is, with potassium permanganate ; while
Messrs. Meyer and Von Recklinghausen employed *acidified*
solutions. We cannot interpret otherwise the expressions :
'' Diese Forscher haben gefunden dass eine Loesung von
uebermangansaurem Kali unter gewissen Bedingungen durch
fein vertheilten Braunstein unter Entwickelung von Sauerstoff
zersetzt wird.'' * * * '' Da nämlich Wasserstoff und
Kohlenoxyd als reducirende Koerper aus der Loesung der
uebermangansäure Braunstein ausscheiden, und dieser, nach
den genannten Autoren, mit Kaliumpermanganat Sauerstoff
unter gewissen Bedingungen entwickeln kann.'' * * *
'' Ob nun die Morse-Hopkins-Walker'sche Erscheinung bei
unseren *Säure*-loesungen eintrete.'' * * * How erroneous
must have been the view which we ascribe to Messrs. Hirtz
and Meyer, on the basis of the above quotations, will appear
when we state that, of the 48 experiments described by Morse,
Hopkins, and Walker, 35 were with *acidified* solutions of per-
manganate.

The second ground which the authors have for believing
that the evolution of oxygen observed by them is not due to
the action of the oxide on the permanganic acid, is one of
great weight, but, to our minds, it is by no means conclusive.
They found that when hydrogen, or carbon monoxide, is ab-
sorbed by a 5 per cent. solution of potassium permanganate
to which has been added 2.5 volume-per cent. of concentrated

sulphuric acid, the evolution of oxygen which occurs *during the absorption* is much more rapid than that which takes place *after the exhaustion* of the gas. This was shown in the following manner : 20 cc. of the acidified permanganate solution and 40 cc. of hydrogen were inclosed in a glass tube and agitated together for twenty-four hours. The tube was then opened and the gas in it displaced by carbon dioxide. On closing the tube again and agitating the contents for another twenty-four hours it was found that only 2.5 cc. of oxygen had been liberated, whereas, according to the experience of Messrs. Meyer and Von Recklinghausen, about 20 cc. of oxygen are evolved when, under similar conditions, 20 cc. of the permanganate solution and 40 cc. of hydrogen are agitated for the same length of time, or even for a shorter time.

It is clear then—and our own results, to be given hereafter, confirm the conclusion—that the evolution of oxygen, which occurs when a gaseous reducing-agent is being absorbed by a concentrated acidified solution of permanganate, is much more rapid than that produced by the oxide, which results from the absorption after the gas has disappeared. It is also more rapid than that observed when an equivalent amount of oxide is produced in the permanganic acid by a liquid reducing-agent, like a solution of manganous sulphate. To us, however, the conclusion that the evolution of oxygen in the two cases is due to wholly different causes is not obvious. We should suspect, rather, that the great initial evolution, observed when hydrogen and carbon monoxide are absorbed, is in some way dependent on the *gaseous* character of these reducing-agents.

We know at present altogether too little regarding the reduction of permanganic acid by the peroxide to give an opinion of any value as to its cause ; and we attach very little value to present speculations on the subject, except so far as they may prove useful in giving direction to a further study of the phenomenon. There is, however, one fact which suggests a provisional hypothesis. We have considerable evidence tending to show that the molecules of the ordinary precipitated peroxides of manganese are quite complex. Perhaps the best evidence of this is to be found in the large

formulas which must be assigned to them in view of the small proportions of water, or of alkalies or other bases which they contain. If they are thus complex, it is conceivable that the tendency toward increasing complexity of constitution should be strong enough to effect the decomposition of permanganic acid with liberation of the superfluous oxygen.

If, in the absence of any other explanation of the reduction of permanganic acid by the peroxide, we accept for the moment the proposed hypothesis, we should ascribe the greater initial evolution of oxygen which is observed when gaseous reducing-agents are used, to the greater initial simplicity of the precipitated peroxide molecules. It is interesting in this connection to notice the volume-relations of the hydrogen absorbed and the oxygen which is liberated during or immediately following the absorption. They are approximately 2 : 1 in all of the experiments of Meyer and Von Recklinghausen. This relation would be explained in terms of the suggested hypothesis by the following reactions :

$$2HMnO_4 + 3H_2 = 4H_2O + 2MnO_2 ;$$
$$2MnO_2 + 2HMnO_4 = H_2O + 2(MnO_2)_2 + 1\tfrac{1}{2}O_2.$$
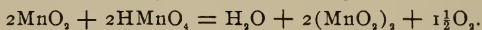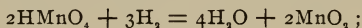
We wish to state again that we have but little confidence in the above speculations. We claim for them this merit only, that, inherently, they are not less improbable than the supposition that the evolution of free oxygen in the two cases under consideration is due to entirely distinct and different causes.

Furthermore, we do not see that the problem can be solved by any simple experimental demonstration. The "experimentum crusis" of Messrs. Hirtz and Meyer[1] established but one thing ; namely, the fact that the evolution of oxygen is phenomenally rapid during or immediately subsequent to the precipitation of the peroxide, when a gaseous reducing-agent is employed, and that fact, taken alone, appears to throw no light on the cause of the evolution. Convinced that, with our slight basis of established fact, discussion is premature, if not profitless, we have undertaken a further study of the reduction of permanganic acid by manganese peroxide. The

[1] Ber. d. chem. Ges., **29**, 2829.

present communication contains the results which were obtained on treating the acid, under equal conditions, with equivalent quantities of hydrogen gas and manganous sulphate. We have thus far experimented with three concentrations of permanganate solution.

The first (A) contained in 1 cc. 2.822 milligrams of $KMnO_4$, equivalent to 5 milligrams of iron. The second (B) was twice as concentrated as A. The third (C) contained in each cc. 51 milligrams of $KMnO_4$, equivalent to 90.38 milligrams of iron. The solutions A and B are of the concentration usually employed in analytical work, while C has about the strength of the 5 per cent. solution which was employed by Messrs. Meyer and Von Recklinghausen and later by Messrs. Hirtz and Meyer.

Great pains were taken to free these solutions from the oxide which is usually found in the commercial salt, and which, as has been shown, is the usual cause of the instability of unfiltered solutions of potassium permanganate. To this end compact asbestos filters were prepared upon perforated porcelain disks placed in the bottom of cylindrical funnels, such as are used in the Gooch method of filtration. Two filters, one placed above the other, were employed. The lower one was closed with a perforated stopper through which the stem of the upper one passed. The filter through which the liquid entered the flask was thus protected from the dust of the air, and the absence of any brown coloration of the lower filter proved the effectiveness of the filtration. We have found these precautions necessary in all quantitative experiments on the reduction of permanganic acid by the peroxide ; since, if they are neglected, it is impossible to ascertain how much of the observed reduction is to be ascribed to the oxide purposely added, and how much to that which was already in the solution.

When solutions of permanganate which contain suspended oxide are heated—especially those which have been acidified —the quantity of the oxide increases very rapidly. We call attention to this fact in connection with the necessity for careful filtration, because it appears to us to have a bearing on some of the results which were obtained by Messrs. Meyer

and Von Recklinghausen. Their acidified solutions were "gut ausgekocht," but it does not appear from their published account that they were filtered.

The volume of permanganate solution used was the same in all experiments; namely, 20 cc. This quantity was enclosed with whatever was to be added to it, in tubes having about 80 cc. capacity, except in the case of solution C, where, owing to the large volume of hydrogen used in some experiments, larger tubes were employed.

Our agitating arrangement was an oscillating table upon which the tubes were held by rawhide lacings. The table was rocked by means of an electric motor and made about 100 strokes per minute. The agitation was continuous, except for occasional interruptions which lasted only a few minutes.

The amount of reduction effected during the agitation was measured by means of standard solutions of oxalic acid and potassium permanganate. This method, with the use of calibrated measuring apparatus, appeared to us quite as accurate as that of determining directly the volume of the liberated oxygen.

Messrs. Meyer and Von Recklinghausen found that when 20 cc. quantities of their 5 per cent. acidified solution of permanganate were agitated with air in closed tubes, they obtained volumes of oxygen ranging from 1.9 to 2.9 cc. An agitation of thirty-three and a half hours gave them 1.9 and 2.2 cc., while in a parallel experiment in which the agitation was continued for eighty-seven hours they obtained only 2.4 cc. In another instance the volumes of liberated oxygen were, at the end of thirty-three and a half hours, 2.8 and 2.9 cc., and at the end of eighty-seven hours, 2.4 cc. Since the decomposition was not appreciably greater in eighty-seven than in thirty-three and a half hours, the authors were led to believe that there is a limit to the reaction by which the oxygen is liberated. These results were not in accord with our own experience. In the first place, we have always found dilute, moderately acidified solutions of permanganate quite stable at ordinary temperatures, provided they were free from oxide. In the second place, in all the cases which have come

under our observation, the decomposition of permanganic acid by the peroxide, which is attended by the liberation of oxygen, has been a continuous reaction, which ceased only when all of the acid had been reduced to the oxide. We had not, however, experimented with solutions as concentrated as that used by Messrs. Meyer and Von Recklinghausen. We therefore inclosed in glass tubes of about 80 cc. capacity 20 cc. portions of permanganate solution C. (51 milligrams of $KMnO_4$ per cc.) and volumes of diluted sulphuric acid, which were equivalent to three times the potassium of the salt. These were agitated for twenty-four hours and then titrated with oxalic acid. The reduction, if any had taken place, was too minute to be detected, nor was any trace of a brown deposit upon the glass to be discovered. The degree of acidity was somewhat greater in our solution than in that employed by Messrs. Meyer and Von Recklinghausen. The difference in the results we must ascribe to the absence of oxide from our solution, and the presence of it in theirs. Their 5 per cent. solution of permanganate was acidified with *concentrated* acid, and then boiled ("gut ausgekocht"), but it does not appear to have been filtered. This treatment leads infallibly to the formation of a large quantity of the oxide; for, when strong sulphuric acid is added to a 5 per cent. solution of the salt, there is a visible precipitation of the peroxide, and the quantity of it is rapidly increased by heating the solution to the boiling-point. Our solution, on the other hand, was filtered with great care, and acidified with diluted acid (3 parts of water to 1 of acid). Moreover, great pains were taken in cleansing the tubes, and to prevent the entrance into them of dust, or any reducing substance.

Having failed to establish the fact of decomposition within twenty-four hour periods, we determined to extend the time of agitation, using varying proportions of acid; and to compare the more dilute solutions A and B with C with respect to stability. The results and the conditions under which they were obtained, are given in tabular form. The numbers given under the head of "volume reduced" signify reduction in accordance with the equation, $2HMnO_4 = H_2O + 2MnO_2 + 3O$, and not total reduction of the permanganic acid.

Permanganate Solution A ; 1 cc. = 5 Milligrams Fe.

Acid.	Time. Hours.	Volume reduced. cc.	Oxygen lost. cc.
O	300	0.12	0.06
O	"	0.11	0.05
= K	"	0.11	0.05
= K	"	0.06	0.03
= 2K	"	0.20	0.10
= 2K	"	0.10	0.05

Permanganate Solution B ; 1 cc. = 10 Milligrams Fe.

Acid.	Time. Hours.	Volume reduced. cc.	Oxygen lost. cc.
O	150	0.02	0.02
O	"	0.04	0.04
= 3K	"	0.10	0.10
= 3K	"	0.10	0.10
= 6K	"	0.08	0.08
= 6K	"	0.10	0.10

Permanganate Solution C ; 5 per cent. $KMnO_4$.

Acid.	Time. Hours.	Volume reduced. cc.	Oxygen lost. cc.
O	150	0.00	0.00
O	"	0.00	0.00
= K	"	0.05	0.45
= K	"	0.04	0.36
= 2K	"	0.02	0.18
= 2K	"	0.11	0.99
= 3K	"	0.40	3.61
= 3K	"	0.22	1.91

It will be seen that none of the three solutions in the neutral
condition lost a measurable quantity of oxygen. As regards
the acidified solutions, it appears that A and B suffered but
little if any decomposition, whether the acid was equivalent
to once or six times the potassium of the permanganate. In
the case of those acidified portions of the solution C, in which the
acid was equivalent to three times the potassium of the perman-
ganate, there was, after an agitation of one hundred and fifty
hours, some evidence of decomposition. A slight deposit of
the brown oxide could be detected upon the glass. This evi-
dence of reduction was wanting in those instances in which
the acid was equivalent to once and twice the potassium.

If we succeeded in our endeavor wholly to exclude the oxide from our solutions, it must be concluded that a 5 per cent. solution of permanganate becomes *per se* somewhat unstable when treated with a quantity of sulphuric acid which is equivalent to three times the potassium of the salt. Our solution C, however, proves itself much more stable than the equally concentrated, but somewhat less acid, solution of Messrs. Meyer and Von Recklinghausen. The most obvious cause of this difference we have already referred to ; namely, the certain presence of suspended oxide in their solution at the beginning of the agitation.

We shall not attempt to explain the fact that Messrs. Meyer and Von Recklinghausen obtained no larger volumes of oxygen after an agitation of eighty-seven hours than were liberated in other experiments during thirty-three and a half hours ; but it occurs to us as something which may have a bearing on the case, that unless proper precautions were taken at the time of transferring the liquid to the tubes, to secure a uniform distribution of all the suspended and precipitated oxide, the quantities of oxide introduced into the different tubes would be likely to vary. That the liberation of oxygen, which occurs when an acidified solution of permanganate containing suspended oxide, is agitated in closed tubes, *does not* cease after a few hours will be amply proved by our later experiments.

The next series of experiments was designed to determine the relative rates of reduction when equal volumes of permanganic acid are agitated : on the one hand, with a given volume of hydrogen ; and on the other, with a quantity of the peroxide which is equal to that which should be produced by the absorption of the hydrogen. Here again, the three solutions, A, B, and C, were employed in the comparison.

The quantities of permanganate to be reduced were in all cases 20 cc. In addition to this, there was added to the hydrogen tubes a quantity of permanganate which would dispose of the gas in accordance with the equation,

$$\mathrm{HMnO_4 + 3H = 2H_2O + MnO_2,}$$

and to the other tubes, enough permanganate and manganous

sulphate to produce the same amount of oxide as would re-
sult from the absorption of the hydrogen, according to the
equation,

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 2HKSO_4 + H_2SO_4 + 5MnO_2.$$
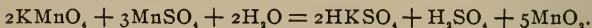
In adding the acid, account was taken of the fact that, in the
case of those tubes in which the peroxide was produced by
the action of the manganous salt on the permanganate, a por-
tion of the required acid had already been introduced through
the sulphate.

In order that the quantity of the gas introduced might be
accurately measured, the tubes designed to receive the hydro-
gen were drawn out, at one end to a capillary and at the other
to a narrow neck, just wide enough to permit the introduction
of liquids from a burette. After introducing the permanga-
nate and the calculated amount of sulphuric acid, the larger
passage was closed before the blast-lamp. The capillary end
was then attached to a Hempel burette filled with mercury,
and a volume of air was withdrawn from the tube which was
equal to that of the hydrogen to be introduced. The burette
was then replaced by one containing hydrogen. By careful
manipulation no especial difficulty was experienced in intro-
ducing quite exactly the required volume of gas. To prevent
the possibility of an explosion of the mixture of gases while
closing the capillary, the tube was so inclined during the
operation, that the liquid in the tube covered the inner end
of the narrow passage. It is hardly necessary to state that,
in estimating the volume of gas required for an experiment,
proper corrections were made for temperature, pressure, and
water vapor.

Through the addition of sulphuric acid to all of the tubes,
and of a standard solution of manganous sulphate to a portion
of them, the original permanganate solutions were somewhat
diluted, and those portions to which the manganous sulphate
was added, to a greater extent than the others; hence, in
order to equalize the conditions as to concentration, it was
necessary to introduce a certain amount of water into the
tubes in which the permanganate was to be agitated with
hydrogen.

The tables which follow give the molecular ratio of the permanganic acid to be reduced to the oxide, the relation of the acid to the potassium of the permanganate, the time of agitation, the percentage reduction of the acid to peroxide, and the volumes of oxygen which were estimated to have been lost.

Permanganate Solution A.

1 cc. equivalent to 5 milligrams of iron.
Volume of original solution to be reduced = 20 cc.
Volumes of hydrogen used = 7.5 cc.
Molecular ratio of $HMnO_4 : MnO_2 = 20 : 12.5$.

Acid.	Time. Hours.	Decomposition by MnO_2 from $MnSO_4$. Per cent.	Volume of oxygen liberated. cc.	Decomposition by MnO_2 from H_2. Per cent.	Volume of oxygen. liberated. cc.
K	150	13.75	0.83	9.59	0.58
K	150	16.50	0.99	8.55	0.51
K	300	21.67	1.29	10.25	0.62
K	600	40.00	2.40	14.34	0.86
2K	150	21.35	1.28	11.60	0.70
2K	150	17.65	1.06	14.00	0.74
2K	300	28.33	1.70	17.00	1.02
2K	300	28.33	1.70	16.67	1.00
2K	600	41.66	2.50	21.08	1.27
3K	150	15.16	0.91	15.83	0.95
3K	150	14.67	0.88	13.50	0.81
3K	300	26.34	1.58	20.83	1.25
3K	300	23.90	1.43	20.74	1.25
3K	600	44.91	2.70	27.00	1.62
3K	24	6.67	0.40	hydrogen not all absorbed.	....
3K	24	5.25	0.32	"	....

It should be remarked with regard to the above, as well as all following similar data that, of the figures expressing reduction of permanganic acid, only those on the same horizontal line are safely comparable. This is true even when the time of agitation is the same in successive experiments, unless the agitation happened to be simultaneous. The rate of the reduction appears to be influenced even by such changes of temperature as are experienced in the laboratory, as, for instance, between day and night.

Permanganate Solution B.

1 cc. equivalent to 10 milligrams of iron.

Volume of original solution to be reduced = 20 cc.

Volumes of hydrogen used = 15 cc.

Molecular ratio of $HMnO_4 : MnO_2 = 20 : 12.5$.

Acid.	Time.	Decomposition by MnO_2 from $MnSO_4$.	Volume of oxygen liberated.	Decomposition by MnO_2 from H_2.	Volume of oxygen liberated.
	Hours.	Per cent.	cc.	Per cent.	cc.
3K	150	17.5	2.1	28.25	3.39
3K	150	15.08	1.81	27.33	3.21
3K	150	17.17	2.06	28.25	3.39
3K	300	33.17	3.98	31.75	3.80
3K	300	32.93	3.95	32.68	3.92
3K	600	61.59	7.38	43.75	5.25
3K	600	62.50	7.50	41.83	5.02
6K	150	18.18	2.18	32.50	3.90
6K	150	19.34	2.32	31.83	3.82
6K	150	20.18	2.42	35.08	4.21
6K	300	31.75	3.81	36.00	4.31
6K	300	31.75	3.81	37.08	4.45
6K	600	60.75	7.28	44.00	5.29
6K	600	75.75	9.08	46.43	5.57
3K	24	3.33	0.40	8.58	1.03
3K	24	4.00	0.48	10.67	1.28

Permanganate Solution C.

1 cc. contained 51 milligrams $KMnO_4 = 89.38$ milligrams Fe.

Volume of original solution to be reduced = 20 cc.

Volumes of hydrogen used = 40 cc.

Molecular ratio of $HMnO_4 : MnO_2 = 20 : 3.784$.

Acid.	Time.	Decomposition by MnO_2 from $MnSO_4$.	Volume of oxygen liberated.	Decomposition by MnO_2 from H_2.	Volume of oxygen liberated.
	Hours.	Per cent.	cc.	Per cent.	cc.
K	150	9.68	10.48	19.93	21.58
K	150	13.75	14.90	19.93	21.58
K	300	22.50	24.38	21.58	23.39
K	300	17.00	18.42	21.75	23.57
2K	150	11.83	12.82	22.50	24.38
2K	150	12.68	13.73	23.93	25.92
2K	300	16.65	18.06	22.08	23.93
2K	300	20.93	22.66	23.33	25.28
3K	150	13.50	14.63	23.74	25.74
3K	150	12.93	14.00	25.83	27.99
3K	300	17.75	19.23	26.75	28.90
3K	24	2.50	2.71	19.58	21.22
3K	24	2.50	2.71	20.18	22.85

The relation of the reduction of the permanganic acid to the time of agitation, as well as to the acidity of the solutions, will be made clearer by the following arrangement, in which the means are given in the case of duplicated determinations:

Solution A.

1. Oxide from $MnSO_4$.

	24 hours. Per cent.	150 hours. Per cent.	300 hours. Per cent.	600 hours. Per cent.
Acid = K	....	15.13	21.67	40.00
" = 2K	....	19.50	28.33	41.66
" = 3K	5.96	14.92	25.12	44.91

2. Oxide from H_2.

Acid = K	....	9.07	10.25	14.34
" = 2K	....	12.08	16.84	21.08
" = 3K	hydrogen not all absorbed.	14.67	20.79	27.00

Solution B.

1. Oxide from $MnSO_4$.

Acid = 3K	3.67	15.56	33.05	62.00
" = 6K	....	19.23	31.75	68.27

2. Oxide from H_2.

Acid = 3K	9.63	27.94	32.22	42.79
" = 6K	....	33.14	36.54	45.22

Solution C.

1. Oxide from $MnSO_4$.

Acid = K	....	11.72	19.75	....
" = 2K	....	12.26	18.75	....
" = 3K	2.50	13.22	17.75	....

2. Oxide from H_2.

Acid = K	....	19.93	21.67	....
" = 2K	....	23.22	22.71	....
" = 3K	19.88	24.82	26.75	....

An examination of the preceding table, for the purpose of comparing the efficiency of manganous sulphate and hydrogen as oxygen liberating agents, shows that, in the case of solutions B and C, the latter is much more active than the former during the first twenty-four hours—that is, during the period

of, or immediately following, the formation of the peroxide which results from the absorption of the gas. This is apparently not true of the very dilute solution A ; for in the experiments upon it, a somewhat smaller reduction of the acid was found than would have been accounted for by the complete absorption of the hydrogen. It cannot, however, be affirmed that the quantity of oxygen liberated was less, in proportion to hydrogen absorbed, in A than in B and C. This is one of the questions to which it is hoped to give further attention in the future. The maximum efficiency of the hydrogen as a quickly acting oxygen-liberating agent, appears to be reached in the case of the nearly saturated solution C, in which the mean reduction during the first twenty-four hours amounted to 19.88 per cent., as against 2.5 per cent. for the manganous sulphate. We call attention to the fact—also noticeable in the results of Messrs. Meyer and Von Recklinghausen—that the reduction of 19.88 per cent. signifies the liberation of 22 cc. of oxygen, a volume which is nearly one-half that of the hydrogen (40 cc.) employed in all the experiments with the solution C.

During the period from twenty-four to one hundred and fifty hours, the oxide produced by hydrogen acted much less rapidly in C than the oxide from the manganous salt. In B —and possibly also in A—the order of efficiency appears to be reversed, the oxide from the hydrogen being the more active one. The latter fact was interesting to us, because it may possibly throw some light upon the important question, whether the phenomenal liberation of oxygen which is observed when hydrogen, or carbon monoxide, acts upon permanganic acid, *attends the absorption of the gas or follows the formation of the oxide produced by the absorption of the same ;* and it suggests a line of investigation which we hope to pursue.

During the period from one hundred and fifty to three hundred hours—also during that from three hundred to six hundred hours, wherever the agitation was so long continued— the oxide from the hydrogen was decidedly less active than that from the sulphate. In one instance, in which a portion

of the solution C had been agitated with hydrogen for three hundred hours, a smaller reduction was found than had occurred in similar experiments during an agitation of one hundred and fifty hours. This discrepancy was explained at the time by the low temperature which prevailed during the agitation of the tube whose contents showed the low reduction.

Assuming that liberation of oxygen in solutions of permanganate or permanganic acid is, in general, due to the presence of suspended oxide, there is no evidence to be found in our results that the reaction has a limit, as believed by Messrs. Meyer and Von Recklinghausen. The evidence to the contrary is very clear in all cases in which the suspended oxide was prepared from manganous sulphate, and also in those cases in which the oxide from hydrogen acted upon solutions A and B. The reduction accomplished in C by the oxide from hydrogen is apparently small during the twenty-four to one hundred and fifty hour and the one hundred and fifty to three hundred hour periods. It is, however, unmistakable, except in the one case which has already been explained. That the percentage reduction for equal periods of time after the first twenty-four hours should be smaller throughout in C than A and B, is easily accounted for by the fact that the suspended oxide in C was relatively less than one-third of that in A and B.

The work which we have here described is only a fragment of a proposed investigation of the reduction of permanganic acid by the peroxide of manganese. The results obtained are not decisive; nor are they even strikingly important in their direct bearing on the question of the cause of the difference between the action of gaseous and liquid reducing agents on permanganic acid. They do, however, suggest certain possible methods of solving the problem.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
May, 1898.

THE ATOMIC WEIGHT OF CADMIUM.[1]

BY H. N. MORSE AND H. B. ARBUCKLE.

Having redetermined the atomic weight of zinc[2] by the method of Morse and Burton,[3] making corrections for the gas which Richards and Rogers[4] found to be retained by the oxide, even at high temperatures, we undertook a similar repetition of the work of Morse and Jones[5] on the atomic weight of cadmium, for the purpose of correcting their results, if cadmium oxide should also be found to retain gas.

Richards and Rogers found no gas in their specimens of cadmium oxide, but as their material had been heated to a higher temperature than is permissible in an atomic weight determination of this metal, we could not be certain that the oxide of Morse and Jones was likewise free from gas. Moreover, it was found by Bucher,[6] in this laboratory, that when a given weight of cadmium oxide, derived from the carbonate, is converted into nitrate, and then again into oxide, the last weight of the oxide is greater than the first. The experience of Bucher points directly to the presence of gas in the oxide from the nitrate.

Another sufficient reason for a revision of the work is to be found in the fact that the results which have been obtained by work upon the halogen salts of cadmium have been throughout notably higher than those based on the weight of the oxide. It appeared desirable to clear up, if possible, the cause of this discrepancy between the two methods.

The metal which was used in this work was the same as that employed by Morse and Jones. It was, in fact, a portion of that prepared for the earlier experiments. It had ·been purified by six fractional redistillations in a vacuum, and examined spectroscopically by Professor Rowland. The details of the distillation process have already been described[7] and need not be repeated.

The nitric acid with which the metal was dissolved was

[2] This JOURNAL, **20**, 195.   [3] *Ibid.*, **10**, 311.

[4] Proc. Am. Acad., **28**, 200.   [5] This JOURNAL, **14**, 261.

[6] Dissertation, 1894, 22.   [7] This JOURNAL, **10**, 311; and **14**, 261.

prepared, as in the earlier work upon zinc and cadmium, by condensing the vapors of the acid upon the surface of a large platinum dish. 15 cc. portions of it, when evaporated in platinum, gave no visible or weighable residue. We deemed it necessary to test the latter condition with unusual care, because of the wide difference between the atomic weights of cadmium and oxygen, and the correspondingly large effect of small errors in weight of material upon the results.

The arrangement of the crucibles in which the metal was converted first into nitrate, then into oxide, and finally weighed, was the same as that formerly used for both cadmium and zinc. It consisted of a small porcelain crucible (No. oo) in which the metal was dissolved, and a larger one (No. II.) in which the smaller one was placed. The smaller, but not the larger, crucible was provided with a lid. The lid and the crucible were, however, separated by means of bent pieces of platinum wire hung over the edge of the latter, thus providing for the free escape of vapors during the solution of the metal and the conversion of the nitrate into the oxide. The glaze was removed from the bottoms of the crucibles, also from the under side of the lid, by means of hydrofluoric acid. The pair of crucibles was weighed together and never separated. A similar, but slightly lighter, pair of crucibles was prepared at the same time to serve as a counterpoise. The platinum hooks belonging to the two sets were brought to nearly equal weight by filing, and then fragments of porcelain were added to the counterpoise until the weights of the two pairs differed by only a small fraction of a milligram. Both were then heated under the same conditions for several hours. The difference between their weights was then carefully determined, after which they were again heated, in order to determine whether the difference remained constant. Throughout the entire determination the two sets of crucibles were treated as nearly alike as the purposes for which they were used would permit ; for instance, if the pair in which the metal had been dissolved was heated, the tare was heated under the same conditions for the same length of time.

Owing to the volatility of cadmium oxide at high temperatures, it was necessary to give careful attention to our heating

arrangements. A small double-walled furnace was made of asbestos board. Two opposite sides were cut away near their centers to permit the entrance of blast flames, and the upper edges were notched to allow the products of combustion to escape. The bath, in which the crucibles previously described were heated, consisted of a large porcelain crucible. This was inserted in a hole in the piece of asbestos board which served as a cover to the furnace. In the bottom of the bath was placed a piece of unglazed porcelain on which the crucibles rested while being heated.

For the air-blast we had a small Root blower which was run by an electric motor; and, as the current was very constant, we were able to maintain quite uniform temperatures. The lamps which we first tried were 2 glass-blower's lamps with 2 jets each. These, with a given adjustment of air and gas-cocks, and speed of the blower, gave us a temperature in the furnace which lay between the fusing-points of sodium chloride (776°) and potassium carbonate (835°). As the former salt fused very readily, while the latter showed no signs of having been softened, we judge that the temperature must have been about 800°. At this temperature it was found practicable to reduce the oxide to constant weight. To ascertain whether a higher temperature might not be employed with safety, we substituted ordinary blast-lamps for those first selected. These gave us a temperature between the fusing-points of pure silver (960°) and potassium sulphate (1066°). But it was found that, at this temperature, specimens of oxide which had been brought to constant weight under the first arrangement began to lose in weight. That the loss was due, in part at least, to sublimation was clear from the fact that portions of the crucible previously white became tarnished with a yellow coating. The blast-lamps were therefore exchanged for those we had used in the first place, and no further change of lamps, or of gas or blast adjustments, was made during the entire work. The temperature was, however, tested from time to time, but always with the same result; sodium chloride fused readily, while potassium carbonate remained unfused after heating for an entire day.

The apparatus for the liberation, collection, and analysis of

the occluded gases was that devised for our earlier work on the atomic weight of zinc.[1] The manipulation of the specimens of oxide and of the gases was also the same as on the former occasion. We stated in our account of the work upon zinc that, in our judgment, the necessary errors connected with the gas analytical part of the determinations could not exceed 1 per cent. of the correction. To test the reasonableness of this estimate, we made determinations of oxygen in 3 specimens of air whose volumes varied between 0.4 and 0.5 cc. The percentages of oxygen found were 20.79, 20.98, and 20.80.

According to C. Langer and V. Meyer[2] nitric oxide is not at all dissociated at temperatures between 900° and 1200°. Emich,[3] on the other hand, states that the dissociation begins at 700°, is small at 900°, is only two-thirds completed at 1200°, and is not finished until the fusing temperature of platinum is reached. The results of both investigations indicate that the temperature of initial dissociation is higher, and its progress slower, than had hitherto been supposed. In view of the fact, therefore, that our oxide was never heated much above 800°, we had to fear the presence in it of oxides of nitrogen, a condition which would have increased very greatly the difficulty of the problem in hand. The following method of testing for the presence of nitric oxide, or other oxides of nitrogen, was adopted : A wide-mouthed salt bottle was moistened on the inside with water ; a crucible containing a quantity of cadmium oxide which had been heated to constant weight was introduced ; a small quantity of dilute sulphuric acid, free from nitric acid, was added to the oxide and the bottle closed. After standing for several hours, the liquid within was tested for nitric acid by the brucine reaction. None was found. In the subsequent work, the acid in which a specimen of oxide had been dissolved, was examined, in every case, by means of the brucine reaction. In no instance, however, was any evidence of the presence of nitric acid found. In view of the fact that about 20 per cent. of the gas retained by the oxide proved to be free oxygen, we

[1] This JOURNAL, **20**, 196.   [2] Pyrochemische Untersuchungen, Seite 66.
[3] Monatshefte für Chemie, **13**, 615.

judged that an examination of the solution, in the manner indicated, was sufficient to demonstrate the presence or absence of nitric oxide or other oxides of nitrogen.

Having converted the dried nitrate into a uniformly dark brown mass, at low temperature, the crucibles were placed in the furnace, previously described, and heated for a period of five or six hours. The tare was then heated for the same length of time, and the weight of the oxide determined. This operation was repeated, without variation, from five to eight times, until no change in the weight of the oxide could be detected after three successive heatings. The crucibles containing the oxide were then brought into our apparatus for dealing with the occluded gases, and there the oxide was treated in the same manner as the oxide of zinc in our earlier work.[1]

When the oxide of zinc is dissolved in dilute sulphuric acid, the evolution of the gas is slow, and continues as long as any of the material remains undissolved. In the case of the oxide of cadmium, on the other hand, a very different phenomenon presents itself. The instant the dilute acid strikes the oxide in the vacuum, there is an almost explosive evolution of gas; and though the solution of the oxide requires some time, but little gas is obtained after the instant of first contact between acid and oxide. The water vapor in the space above the crucibles condenses to a visible mist which settles upon the interior glass surfaces. The disturbance in the oxide, during this sudden liberation of gas, is so great that we were obliged to take measures to prevent it from being thrown out of the crucibles. The gas was collected and analyzed in precisely the same manner as that obtained from the oxide of zinc.

The results of the 9 determinations which were made are presented in the following table :

[1] This JOURNAL, **20**, 195.

	Weight of cadmium.	Weight of oxide.	Uncorrected atomic weight.	Volume of gas (st. cond). cc.	Percentage of oxygen.	Corrected atomic weight.
1	1.93188	2.20764	112.092	0.574	21.25	112.392
2	1.67935	1.91910	112.074	0.480	25.16	112.365
3	1.48430	1.69620	112.076	0.441	19.95	112.376
4	1.36486	1.55972	112.071	0.402	18.33	112.368
5	1.50295	1.71744	112.112	0.419	21.95	112.394
6	1.43804	1.64330	112.093	0.431	18.56	112.395
7	1.44041	1.64604	112.079	0.406	20.93	112.365
8	1.45938	1.66771	112.082	0.421	21.85	112.375
9	1.40379	1.60420	112.076	0.390	19.50	112.359

Mean = 112.084   Mean = 112.377

The uncorrected result, 112.084, is very close to the value 112.071 (112.06 with all corrections applied to weighings) which was obtained by Morse and Jones[1]; while the corrected result, 112.377, accords equally well with the mean values 112.39 and 112.38, which were obtained by Bucher[2] in his work upon the chloride and bromide of cadmium.

The relation of the volume of the occluded gas to the weight of the oxide is remarkably constant, as will be seen from the following table, in which is given for the individual determinations the volume of gas per gram of oxide:

	cc.		cc.		cc.
1	0.260	4	0.258	7	0.246
2	0.250	5	0.244	8	0.252
3	0.260	6	0.262	9	0.243

The mean volume of the gas per gram of the oxide is 0.253 cc. as against 0.301 for the oxide of zinc.

A few experiments were made in order to determine whether the gas could be extracted without dissolving the oxide. The first of these was to ascertain whether the oxide, under water, would lose any portion of its gas when left for a long time in a vacuum. The bulb containing the acid was emptied and thoroughly washed with pure water, and then filled with water of perfectly neutral reaction. The water in the bulb was exhausted by occasional pumping until no trace of air could be obtained from it. A specimen of the oxide which had been heated for the usual length of time, was then

brought into the apparatus and covered with water. After exhausting again as completely as possible, connection with the pump was cut off and the oxide allowed to stand undisturbed for three days in the vacuum. Not a trace of gas was liberated. The next experiment was to determine whether boiling water would liberate the gas. A specimen of the oxide, weighing 1.4134 grams, which had been heated the usual length of time, but not tested as to the constancy of its weight, was heated for six hours under boiling water, and then dissolved in a vacuum. The volume of gas obtained was 0.403 cc., or 0.284 cc. per gram of the oxide. It appears, therefore, that the oxide of cadmium does not lose its gas, either under water in a vacuum or under boiling water at atmospheric pressure.

Two experiments were made to determine whether oxide of cadmium still retains gas when heated to a temperature at which it begins to volatilize. The oxide was reduced to constant weight, and then, by substituting common blast-lamps for those ordinarily used, the temperature of the furnace was raised to a point lying between the fusing temperatures of pure silver (960°) and potassium sulphate (1066°). At this temperature the oxide lost in weight, very slowly but, nevertheless, steadily ; and the white porcelain of the crucibles became tarnished with a yellow coating, proving unmistakably that sublimation had begun.

Both samples of the oxide were four times reheated, each time for six hours, and weighed after each heating. The separate losses were very minute ; and, altogether, they amounted only to 1 milligram in one case, and to 0.57 milligram in the other, showing that we had not exceeded the temperature of initial volatilization. When these specimens of oxide were afterwards dissolved in a vacuum, one of them gave 0.240 cc. and the other 0.247 cc. of gas per gram of oxide.

The gas from the oxide of cadmium was examined spectroscopically, after removal of the oxygen, and found to be nitrogen.

Chemical Laboratory,
Johns Hopkins University,
May, 1898.

CVIII.—A TABLE OF ATOMIC WEIGHTS.[1]

By Theodore William Richards.

Since no natural constants are more used by chemists than the atomic weights, it is a matter of great importance for every one, from tne chemical philosopher to the practical analyst, to have a convenient table of them always at hand. Unfortunately the present state of our science makes the selection of the values often a matter of personal opinion ; and because this is the case, it is well that many of those who have had experience in accurate quantitative analysis should express their views. Hence arose the present work, which was begun solely for use in Harvard College.

It is true that an accurate table of atomic weights may sometimes be less appropriate for the calculation of analyses than an inaccurate one, for the constant errors of any one process are eliminated as much as possible from the accurate table, and, moreover, all the results are reduced to the vacuum standard. Of course neither of these refinements is to be expected in common work, although many uncorrected methods may yield results which are very consistent among themselves. Obviously the best table for the practical calculation of analyses would be a list of factors, in which each quantity had been found empirically according to precisely the method which is to be employed in the analysis of an unknown substance.[2] Since, however, the errors of ordinary work often eliminate one another, and since such a table of empirical factors would have to be accompanied by exceedingly minute directions, the scientifically accurate table of atomic weights is generally the most convenient substitute for the factors demanded by the analyst, as well as the most suitable basis for theoretical considerations concerning the periodic system of the element.

In the compilation of the following table the chief emphasis has been laid on the probable chemical accuracy of the processes involved in each case. The search for possible

[1] Presented to the American Academy of Arts and Sciences, March 9, 1898.
[2] Compare Seubert : Ber. d. chem. Ges., **21**, 2180.

causes of constant chemical error has usually furnished the evidence, if any evidence was to be obtained, upon which has been based the sometimes very puzzling decisions between conflicting data. For example, the possible occlusion of foreign matters by many precipitates has always been borne in mind, as well as the fact that crystals obtained from aqueous solutions usually retain with great obstinacy important amounts of mother-liquor enclosed within their structure. Oxides and other substances obtained by ignition often have a tendency to occlude traces of other materials remaining from their mother compound ; of course the possibilities of such a serious error must be carefully weighed in each case. Most experimenters upon the volumetric ratio of silver to the chlorides have produced erroneous data, through lack of knowledge of the dangers of this apparently simple process. These results must then be given small weight, no matter how concordant they may seem. The solubility of glass and porcelain, as well as nearly all precipitates, is another frequently overlooked source of grave complications, and so is the action of many substances upon their containing vessels at high temperatures. The fact that in some cases the necessary methods of calculation greatly magnify the experimental error was not forgotten. These and many other equally obvious minor principles have served as the guides in the selection of the figures below ; but of course the results cannot be considered ultimate. ''Post-mortem examinations are often unable to detect the more subtle poisons.'' In many cases much more experimental work is needed, not only to secure new data, but also to show where the old are in error. While, however, it is very important to show such falsity, the attempt to counteract it numerically by the application of small corrections, is a dangerous remedy ; for minor conditions often seriously modify the minor corrections. In such cases wholly new data must usually be obtained, and these must be corrected, if correction is necessary, by him who is familiar with every step of the processes involved.

One is continually reminded, as he studies the conflicting evidence of the words of Ostwald : ''Differenzen sind nicht selten, und mahnen ernstlich an die Unvollkommenheit

menschlicher Arbeit, aber auch an die Verantwortung, welcher jeder übernimmt, welcher einen numerischen Wert der Oeffentlichkeit mitteilt.''[1]   This responsibility is not always realized by eager investigators, who seek to make up for a possible lack of quality by a superabundance of quantity. ''A single determination, well worked out, is better than twenty incomplete ones. Too much cannot be said against the multiplication of incomplete or carelessly obtained data ; for such data carry with them not only uncertainty and confusion in the present, but also additional labor for a reviser in the future.''[2]   Every reaction must be assumed to involve some constant error, and every substance must be assumed to contain some constant impurity, until a proof of the contrary is obtained. Our wofully discordant data furnish a heavy presumption against almost any chemical method, when greater accuracy than one part in four or five hundred is desired.

The standard $O = 16.000$ is adopted below, as likely to be the most convenient for many years to come.[3]   The last figure of each number given in the following table cannot be considered in any case certain. It is often probably not much more than one unit in error, although the uncertainty may amount to as much as six or eight units in some cases. Of course the decimal notation does not admit of closer indications without an individual explanation in each case. For example : iron, germanium, and gallium are given in the table as 56.0, 70.0, and 72.5 respectively. The first is probably known within 0.1 or 0.2, while the other two may easily be 0.5 in error ; but the method of expressing the results does not admit of this grade of distinction.

The aim has been to construct a convenient working table, which shall carry with it all that is trustworthy, and nothing that is unnecessary. It is almost needless to state that the well-known standard works of Clarke, Meyer and Seubert, Ostwald, Van der Plaats, and others, have been freely consulted in the preparation of this table, as well as many of the original papers.

[1] Ztschr. phys. Chem., **3**, 143.   [2] Proceedings Amer. Acad., **31**, 99 ; **26**, 294.
[3] Compare F. W. Küster : Ztschr. anorg. Chem., **14**, 251.

Especially am I indebted to Professor Clarke for his latest gigantic collection of data and results,[1] which would have made the present table a work of supererogation, if he had viewed the subject from a somewhat less mathematical standpoint. Professor Clarke's method of decision places the credit with the skilful manipulator; I have striven to give the thoughtful chemist who is not so clever with his hands the credit which I think belongs to him. The fact that the two tables usually agree is due either to the best methods having fallen into the best hands; or to Professor Clarke's having wisely forsaken the rigid application of his principle; or else, especially in the case of the rare metals, to the lack of data affording room for intelligent difference of opinion. Among the seventy-four atomic weights given in the table, only seven differ enough from the values computed by Clarke to excite remark. It seems fitting to give a brief statement of the reasons for the differences in those seven cases, leaving the details of reasoning about the other sixty-seven elements unpublished. The elements mentioned are antimony, cadmium, calcium, magnesium, platinum, tungsten, and uranium.

It is not my purpose to enter at length into the discussion of the antimony problem. Much of the voluminous work upon this subject is now rejected by common consent. The work of Bongartz,[2] sometimes accepted as the best because it is the most recent, has the grave faults inherent in all methods which involve the precipitation of baric sulphate. Among all the published data Cooke's analyses of antimonious bromide[3] ($Sb = 119.92$) seem to me the most satisfactory, because of the admirable fitness of argentic bromide for quantitative work, and because of the many precautions used in both preparation and analysis. Cooke's[4] and Schneider's[3] work upon the sulphide ($Sb = 120.5$) are perhaps the next in order; but Cooke's work upon this subject was far less satisfactory than his work on the bromide. Accordingly, the value 120.0 is given as the atomic weight of antimony in the accompanying table, instead of 120.43, computed by Clarke.

[1] Smithson. Misc. Coll., Constants of Nature, **5**, (1897).

[2] Bongartz : Ber. d. chem. Ges., **16**, 1942, (1883).

[3] Cooke : Proc. Am. Acad., **5**, 13, (1877).

[4] Schneider : Pogg. Ann., **98**, 293, (1856); Jour. prakt. Chem. (2), **22**, 131, (1880).

Although the atomic weight of cadmium has been the subject of many investigations, it is still far from certainly established. Many reasons combine to make me think that the highest of the published values are the most accurate. Dumas'[1] work upon the chloride of cadmium led to the value 112.23 ; but his method of investigating chlorides sometimes gave him too low results.[2] V. Hauer[3] and Partridge[4] found cadmium equal to less than 112 by heating cadmic sulphate in a stream of hydric sulphide, but there is no proof that their initial substance was thoroughly dried. On the other hand, Bucher's conversion of cadmic sulphate into the oxide led to the value 112.36, which Bucher regards as the minimum.[5] This method is one in which the tendency of the oxide to retain sulphuric acid is approximately neutralized by the tendency of the sulphate to retain water; this fact, is demonstrated by Baubigny's[6] good results on zinc, nickel, and aluminium, as well as Marignac's[7] on magnesium. The results of Lenssen,[8] Partridge, Morse and Jones,[9] and Bucher, involving the use of cadmic oxalate, all in the neighborhood of 112, are likely to be too low because of the great difficulty of freeing this substance from water. Morse and Jones have clearly indicated this and other possible causes of error. Moreover, I doubt very much if it is possible to prepare the oxalate free from the nitrate by precipitation from solutions containing cadmic nitrate. The method of calculation magnifies either error by introducing it in opposite directions into the numerator and denominator. Bucher's extended work casts grave doubts upon cadmic oxide (used by Morse and Jones, and Lorimer and Smith)[10] as a suitable substance to serve for a basis of operations. On the other hand, the work of Huntington[11] and

[1] Dumas : Ann. Chem. (Liebig), 113, 27, (1860).

[2] See Proceedings Am. Acad., 30, 371. Cases in point : barium, strontium, sodium, and tin.

[3] Von Hauer : Jour. prakt. Chem., 72, 350, (1857).

[4] Partridge : Am. Jour. Sci. (3), 40, 377, (1890).

[5] J. E. Bucher : Johns Hopkins Inaug. Dissertation, Baltimore, (1892).

[6] Baubigny : Compt. rend., 97, 906, 951, 1369, (1883).

[7] Marignac : See under magnesium, later in this paper. Compare Proceedings Am. Acad., 26, 260, 273 ; 31, 160.

[8] Lenssen : Jour. prakt. Chem., 79, 281, (1860).

[9] Morse and Jones : This JOURNAL, 14, 260.

[10] Lorimer and Smith : Ztschr. anorg. Chem., 1, 364.

[11] Proceedings Am. Acad., (1881), p. 28.

Bucher with a bromide (a very satisfactory substance as to its preparation because it may be sublimed, and as to its analysis because of the insolubility of argentic bromide), and that of Bucher with cadmic chloride, point toward 112.3 or 112.4 as the probable figure. The electrolytic work of Hardin[1] upon these compounds, performed unfortunately with small amounts of material, is nevertheless in favor of the lower value, 112.0, so that any value adopted must be uncertain. Clarke computes 111.95; for the following table, 112.3 has been chosen.

There is good reason for believing that Clarke's value for calcium (40.07) is probably too high. The only determinations worth considering are those of Erdmann and Marchand upon the composition of Iceland spar, and only one out of their thirteen experiments is corrected for known causes of constant error.[2] This experiment, which really constitutes the sum and substance of our pseudo-accurate knowledge of a very important quantity, makes calcium almost exactly 40.0. Obviously but little confidence may be placed in such meagre material; it is surprising enough that so common an element has remained forty years untouched on so unsatisfactory a basis. An extended investigation, now well advanced in this laboratory, has as its object the securing of less impeachable data upon the atomic weight of this frequently appearing constituent of the universe.

Marignac's[3] results from the quantitative ignition and synthesis of magnesic sulphate, processes in which the constant errors are likely to eliminate one another, have been so completely confirmed by the recent work of Richards and Parker,[4] that magnesium is represented by the figure 24.36 in the table. The results of the syntheses of magnesic oxide by Burton and Vorce[5] have been shown by Richards and Rogers[6] to be under the cloud of a serious possible constant error, and no other results offer weighty evidence against the value just named.

1 Hardin : Jour. Am. Chem. Soc., **18**, 1016, (1896).

2 Erdmann and Marchand : Jour. prakt. Chem., **50**, 237, (1850).

3 Marignac : Arch. Sci. Phys. et Nat. (3), **10**, 206.

4 Richards and Parker : Proceedings Am. Acad., **32**, 53 ; Ztschr. anorg. Chem., **13**, 81, (1896).

5 Burton and Vorce : This JOURNAL, **12**, 219, (1890).

6 Richards and Rogers : Proceedings Am. Acad., **28**, 200.

An important deviation from the usually accepted figures is to be seen in the value assigned to platinum below. Our knowledge of the atomic weight of this element depends chiefly upon the elaborate and carefully executed work of Seubert[1] and Halberstadt,[2] and the only question is how this is to be interpreted. These chemists studied the platin-chlorides and platinbromides of potassium and the platin-chloride of ammonium, weighing these compounds and some of the products of their decomposition. The careful study of the results shows at once that some source of error lies hidden in all the data, for the various ratios are not wholly consistent, even in any one series. Any value from 194.7 to 196.0 may be obtained from the figures,[3] the results of Seubert's work being the least discordant among themselves. Dittmar and M'Arthur[4] explain the discrepancy in the case of potassic platinchloride by assuming that the complex salt contains traces of hydroxyl replacing the halogen and traces of hydrogen replacing the potassium, as well as a small amount of extra occluded potassic chloride. They adduce experimental evidence in proof of this view, but Seubert showed in his reply[5] that their hypotheses can hardly be applied to his determinations. Most of Seubert's and Halberstadt's inconsist-encies may be explained by the supposition that the complex salts, like all substances crystallized from aqueous solution, contain certain traces of mother-liquor held in minute cells within the crystal structure, and that these traces of water are not free until the substance is disintegrated. I have accu-mulated a large amount of experimental evidence, soon to be published, upon this subject. Water is one of the most dan-gerous, although one of the least heeded, impurities in this kind of work ; and in my opinion it is responsible for the lack of agreement in this case. Hence the best data for the calcu-lation of the atomic weight of platinum seem to be those con-cerning the relation of the metallic platinum to the potassic chloride or potassic bromide formed by the decomposition of

[1] Seubert : Ber. d. chem. Ges., **14**, 865, (1881).
[2] Halberstadt : *Ibid.*, **17**, 2962, (1884).
[3] Clarke : Recalculation, (1897), p. 334.
[4] Trans. Roy. Soc. Edinburgh, **33**, Part II, 561, (1887).
[5] Ber. d. chem. Ges., **21**, 2179.

the complex salts, for the water must surely have been expelled from these products of the ignition. According to Clarke[1] potassic platinchloride yields 40.101 per cent. of platinum and 30.671 per cent. of potassic chloride,—the means of the closely agreeing results of Seubert and Halberstadt,—while according to Halberstadt potassic platinbromide yields 25.915 per cent. of platinum and 31.591 per cent. of potassic bromide. Disregarding the weight of the complex salt, and assuming that $KCl = 74.595$, and $KBr = 119.095$, it is easy to calculate the respective values 195.06 and 195.39 for platinum. The mean of these two values, 195.2, is given below, instead of Clarke's 194.89. The possible occlusion of potassic halide by the complex salt may render even 195.2 too low; but more investigation is evidently needed to prove this.

The same errors may enter into the work on other platinum metals; indeed Seubert[2] admits that traces of water were contained in some of his salts, but he applies no correction for this serious cause of inaccuracy. Since, however, Clarke's method of combining the discordant results seems more nearly to eliminate the error in these cases, his values for these elements are but little changed in the following table.

Feeling wholly unable to decide the present controversy between the two conflicting values (184.9 and 184.0) now proposed for tungsten, I have chosen the mean 184.4 as a compromise which cannot be much more than 0.3 per cent. out of the way.[3]

Uranium, the highest of all the atomic weights, is one of the least satisfactorily determined. Recent investigation upon this subject at Harvard seems to show that all the published data are complicated by constant errors, which, however, sometimes partly eliminate one another; accordingly the round number 240, instead of Clarke's 239.59, is printed in the table. The discussion is better deferred until our work has taken more definite shape.

Besides these seven elements, there are seventeen more whose atomic weights, as given in the following table, differ from the results of Professor Clarke's computations by one

[1] Recalculation, page 333. [2] Ann. Chem. (Liebig), **261**, 262.
[3] Compare Hardin: J. Am. Chem. Soc., **19**, 657, (1897).

part in a thousand or more. As none of the seventeen values is known certainly to within one part in five hundred, and some of them are probably at least as much as one per cent. in error, differences in these cases will excite no especial remark. The elements are: cerium, columbium, erbium, gadolinium, gallium, glucinum, indium, lanthanum, neodymium,[1] osmium, palladium, praseodymium, samarium, scandium, thorium, ytterbium, and zirconium. This is by no means a complete list of the uncertain elements, but only of those for which the data admit of slightly different interpretations.

It is rather unfortunate that most classified tables of the elements omit the fractional parts of the atomic weights, for these fractions will undoubtedly play an essential part in the ultimate solution of the de-Chancourtois-Newlands-Mendeléeff-Meyer mystery. In order to present a modern table which will supply these omissions, as well as afford at a glance an approximate idea of the probable error in each case, I have repeated the values in the natural order. From the classified table have been omitted several elements whose atomic weights and properties are uncertain; their presence in the system serves rather to obscure well-known relations than to elucidate new ones. That this procedure is an omission of incompleteness is evident; the last part of the table is at best a lame affair. The form proposed by Thomsen[2] is perhaps the most generally satisfactory of the current modes of arrangements, but his last row is unwieldy both for printing and for thinking. In the accompanying table a compromise has been adopted which cannot fail to be comprehensible; it is not my purpose here to enter into the arguments regarding the adequacy of the various forms.

This table will be reprinted, with any changes which may

[1] Since the publication of this paper in the Proceedings of the American Academy, H. C. Jones has published a research upon the "dymia" which far exceeds in accuracy and completeness the vague statements of their first separator. Oddly enough the new values are the old ones interchanged. While it is impossible to say how nearly the new figures represent the peculiarly elusive values in question, they carry with them much greater weight than the old ones, and are given, as far as the first decimal place, in the following table. See this volume, p. 345. The value 142 for the mixture "didymium" is also given for convenience in the calculation of analyses in which it is not possible to separate the twins.

[2] Ztschr. anorg. Chem., 9, 190.

be necessary, every year. Since the commencement of the work I have been glad to hear of the appointment of a committee by the German Chemical Society to accomplish a similar purpose, the American Chemical Society having for several years possessed such a committee. The matter cannot receive too much intelligent examination.

A TABLE OF ATOMIC WEIGHTS

OF SEVENTY-FOUR ELEMENTS.

Compiled in March, 1898, from the Most Recent Data.

Name.	Symbol.	Atomic weight.
Aluminium	Al	27.1
Antimony	Sb	120.0
Argon	A	39.9?
Arsenic	As	75.0
Barium	Ba	137.43
Beryllium	Be = Gl	9.1
Bismuth	Bi	208.0
Boron	B	10.95
Bromine	Br	79.955
Cadmium	Cd	112.3
Caesium	Cs	132.9
Calcium	Ca	40.0
Carbon	C	12.001
Cerium	Ce	140.0
Chlorine	Cl	35.455
Chromium	Cr	52.14
Cobalt	Co	59.00
Columbium	Cb = Nb	94.0
Copper	Cu	63.60
"Didymium"	Nd + Pr	142 ±
Erbium	Er	166.0
Fluorine	F	19.05
Gadolinium	Gd	156.0 ?
Gallium	Ga	70.0
Germanium	Ge	72.5
Glucinum	Gl = Be	9.1
Gold	Au	197.3
Helium	He	4.0 ?
Hydrogen	H	1.0075
Indium	In	114.0
Iodine	I	126.85
Iridium	Ir	193.0
Iron	Fe	56.0
Lanthanum	La	138.5

Name.	Symbol.	Atomic weight.
Lead	Pb	206.92
Lithium	Li	7.03
Magnesium	Mg	24.36
Manganese	Mn	55.02
Mercury	Hg	200.0
Molybdenum	Mo	96.0
Neodymium	Nd	143.6
Nickel	Ni	58.70
Niobium	Nb = Cb	94.0
Nitrogen	N	14.045
Osmium	Os	190.8
Oxygen (standard)	O	16.000
Palladium	Pd	106.5
Phosphorus	P	31.0
Platinum	Pt	195.2
Potassium	K	39.140
Praseodymium	Pr	140.5
Rhodium	Rh	103.0
Rubidium	Rb	85.44
Ruthenium	Ru	101.7
Samarium	Sm	150.0
Scandium	Sc	44.0
Selenium	Se	79.0
Silicon	Si	28.4
Silver	Ag	107.93
Sodium	Na	23.050
Strontium	Sr	87.68
Sulphur	S	32.065
Tantalum	Ta	183.0
Tellurium	Te	127.5
Terbium	Tb	160.0
Thallium	Tl	204.15
Thorium	Th	233.0
Thulium	Tu	170.0 ?
Tin	Sn	119.0
Titanium	Ti	48.17
Tungsten	W	184.4
Uranium	U	240.0
Vanadium	V	51.4
Ytterbium	Yb	173.0
Yttrium	Yt	89.0
Zinc	Zn	65.40
Zirconium	Zr	90.5

THE CLASSIFICATION OF THE ELEMENTS.

H = 1.0075

Li = 7.03	Na = 23.050				
Gl = 9.1	Mg = 24.36				
B = 10.95	Al = 27.1				
C = 12.001	Si = 28.4				
N = 14.045	P = 31.0				
O = 16.000	S = 32.065				
F = 19.05	Cl = 35.455				

K = 39.140	Rb = 85.44	Cs = 132.9	......	......
Ca = 40.0	Sr = 87.68	Ba = 137.43	......	......
Sc = 44.0	Y = 89.0	La = 138.5	......	......
Ti = 48.17	Zr = 90.5	Ce = 140.0	......	Th = 233.0
V = 51.4	Cb(Nb) = 94	......	Ta = 183.0	U = 240.0
Cr = 52.14	Mo = 96.0	......	W = 184.4	
Mn = 55.02	......		......	

Fe = 56.0	Ru = 101.7	......	Os = 190.8
Co = 59.00	Rh = 103.0	......	Ir = 193.0
Ni = 58.70	Pd = 106.5	......	Pt = 195.2

Cu = 63.60	Ag = 107.93	......	Au = 197.3
Zn = 65.40	Cd = 112.3	......	Hg = 200.00
Ga = 70.0	In = 114.0	......	Tl = 204.15
Ge = 72.5	Sn = 119.0	......	Pb = 206.92
As = 75.0	Sb = 120.0	......	Bi = 208.0
Se = 79.0	Te = 127.5?	......	
Br = 79.995	I = 126.85	......	

Unclassified :

Helium = 2.0 or 4.0?	Gadolinium = 156.0
Argon = 19.94 or 39.9?	Terbium = 160.0
Praseodymium = 140.5	Erbium = 166.0
Neodymium = 143.6	Thulium = 170.0
Samarium = 150.0	Ytterbium = 173.0

Anomalous :

Cobalt = 59.00
Nickel = 58.70
Tellurium = 127.5

LXI. — RESEARCHES ON THE CYCLO AMIDES: α-KETOBENZMORPHOLINE AND α-BENZ-PARAOXAZINE DERIVATIVES.

By H. L. Wheeler and Bayard Barnes.

α-Ketobenzmorpholine, or from its method of preparation called orthoaminophenoxyacetic acid anhydride, has the structure of a cyclo amide and should act like an acid amide or, in other words, as if it were a derivative of the two forms,

$\overline{NH}$ — $\overline{CO}$ and $\overline{N}$ = $\overline{COH}$. The literature on this compound would seem to indicate that it is a very inactive substance, since no derivatives of it have hitherto been prepared. It will be shown, however, in this paper, that this compound behaves like an amide and yields derivatives which, in their properties, are closely related to the corresponding compounds of formanilide.

Orthoaminophenoxyacetic anhydride was first obtained by Fritzsche[1] by reducing orthonitrophenoxyacetic acid with stannous chloride. According to Thate,[2] this compound is not obtained pure by Fritzsche's method, but is best prepared by reducing the nitro compound with iron and acetic acid.

Aschan[3] obtained this so-called anhydride from orthoaminophenol and chloracetyl chloride. He states that concentrated acids and alkalies have no effect on the substance, but that it reacts energetically with phosphorus pentachloride, with at least partial decomposition.

The latest work on the subject is that of Duparc.[4] At Gräbe's suggestion he undertook the examination of this anhydride in order to determine which of the following formulas is to be assigned to the substance:

$$C_6H_4 \Big\langle \begin{array}{c} O - CH_2 \\ | \\ NH - CO \end{array} \quad \text{or} \quad C_6H_4 \Big\langle \begin{array}{c} O - CH_2 \\ | \\ N = COH \end{array}.$$

(α-Ketobenzmorpholine.)   (α-Oxybenzparaoxazine.)
      I.   II.
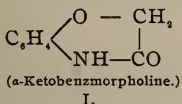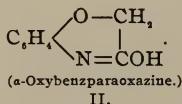
[1] J. prakt. Chem. [2], **20**, 288.
[2] Ibid. [2], **29**, 180.
[3] Ber. d. Chem. Ges., **20**, 1523.
[4] Ibid., **20**, 1943.

Duparc found that the material was not acted on by acetic anhydride even at 180°, and since he did not succeed in obtaining a reaction with methyl iodide or nitrous acid he abandoned the subject.

We have taken up the work at this point and find that a sodium and silver salt of this cyclo amide can easily be prepared, and that the action of alkyl iodides on these salts give two series of isomeric alkyl compounds. Those obtained from the sodium salt have the alkyl group joined to nitrogen and are to be considered as α-ketobenzmorpholine derivatives, Formula III., while those from the silver compound have the alkyl group attached to oxygen, and are cycloimidoesters or benzparaoxazine[1] derivatives, Formula IV.
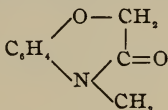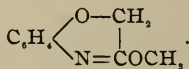
III.   IV.

The structure of these compounds is settled from the following : The product obtained by the action of methyl iodide on the sodium salt gave on prolonged heating with concentrated hydrochloric acid, at a high temperature, orthomethyl-aminophenol, $C_6H_4\begin{smallmatrix}OH\\NHCH_3\end{smallmatrix}$, thus showing, in the case of the sodium salts, that the alkyl groups attach themselves to nitrogen.

On the other hand, the products obtained from the silver salt, even on treating with cold dilute hydrochloric acid, immediately regenerate α-ketobenzmorpholine. This instability in the presence of acids, being a characteristic property of substituted imido esters, shows that in this case the alkyl groups are attached to oxygen.

[1] Hitherto only two benzparaoxazine derivatives have been prepared. The compound obtained by reducing orthonitrophenylacyl ether, *i. e.*, $C_6H_4\begin{smallmatrix}O-CH_2\\N=C.C_6H_5\end{smallmatrix}$, and the analogous methyl derivative, are sometimes called β-phenyl and β-methylbenzparoxazines (Ber. d. chem. Ges., **23**, 172). From analogy with the quinoline derivatives, quinaldine, for example, being called α-methylquinoline, these compounds should be termed α- and not β-derivatives. The latter nomenclature is used in this paper.

It will be noticed that the above behavior of the sodium and silver salts of α-ketobenzmorpholine is perfectly analogous to that of the salts of the anilides. Indeed the analogy by no means ends in this behavior but extends also to the derivatives. The cycloimido esters obtained from the silver salt of α-ketobenzmorpholine have strong, peculiar odors, and decompose into ketobenzmorpholine on exposure to the air; the isomeric compounds have no odor and are stable on exposure. The compounds from the silver salt behave precisely like the isoanilides or substituted imido esters, not only in being immediately decomposed by acids but also inasmuch as they react with bases, at ordinary temperature, giving amidines. These amidines, some of them difficult to crystallize, give well-crystallized salts.

Again, the silver salt of α-ketobenzmorpholine reacts with acyl chlorides, like the silver salts of the anilides, giving well-crystallized acyl derivatives. These derivatives have the acyl group attached to nitrogen. It is noteworthy that, in spite of the failure of Duparc to obtain an acetyl derivative by means of the keto compound and acetic anhydride, such a compound results, with evolution of heat, from the silver salt. Moreover, this acetyl compound is so stable that it can be crystallized from water without decomposition.

It is now shown that α-ketobenzmorpholine behaves precisely like formanilide, and therefore the normal structure is to be assigned to this cyclo amide, *i. e.*, Formula I.

That the amides in general are derivatives of the structure $-\overset{|}{N}H-\overset{|}{C}O$ and not $-N=\overset{|}{C}OH$, or, in other words, that they have the keto and not the enol form follows from the behavior of their oxy compounds.

It is well known that the oxy acids, especially the gamma and delta derivatives, readily separate water, giving lactones. If the amides had the second of the above structures they would be imido acids and their oxy compounds would be expected to separate water, like the oxy acids themselves, giving imidolactones; *viz.*,

$$\underset{\diagdown OH}{HOCH_2CH_2CH_2C{=}NH} \;\longrightarrow\; \underset{\llcorner\!-\!-O\!-\!-\!\lrcorner}{CH_2CH_2CH_2C{=}NH.}$$
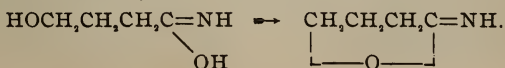
Imidolactones have not yet been obtained. The oxyamides do not form anhydrides in this manner. For example: gamma-oxyvaleramide results by heating gamma-oxyvalerianic anhydride or the ester with ammonia to 100°. On boiling this oxyamide it slowly decomposes, giving off ammonia and not water; indeed some of these oxyamides boil unaltered. These facts not only show that the acid amides have the normal structure, but they also dispose of the theory that in these compounds the enol and keto form exist in a state of equilibrium.

Lachmann[1] in his interesting paper on the constitution of the acid amides concludes that acetamide and benzamide have hydroxyl groups because they *immediately* give off hydrogen chloride with phosphorus pentachloride. Oxamethane does not immediately decompose in this manner but gives an amide chloride.[2] He, therefore, concludes that oxamethane has a keto group, and that these results point to a division of the amides into two groups, etc. The following considerations show, however, that this is not the true explanation of the behavior of these amides with phosphorus pentachloride. We know from the work of Wallach,[3] Lengfeld and Stieglitz,[4] and others, that the grouping V. (below) is very unstable, the grouping VI. being more stable. It has been shown in papers from this laboratory that the more negative the character of the molecule in this or the analogous grouping VII., the less stable are the compounds. What applies to grouping VII would therefore apply in greater force to grouping V.

$$RC \begin{matrix} \diagup NHR' \\ \diagdown Cl_2 \end{matrix} , \quad RC \begin{matrix} \diagup NR' \\ \diagdown Cl \end{matrix} , \quad RC \begin{matrix} \diagup NR' \\ \diagdown OC_2H_5 \end{matrix} .$$

$$\text{V.} \qquad\qquad \text{VI.} \qquad\qquad \text{VII.}$$
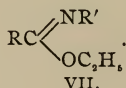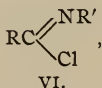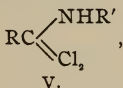
We now have the true explanation of Lachmann's results. The amide chlorides of acetamide and benzamide are far more negative than the amide chloride of carbonic acid or its ester-amide oxamethane, and, as would be expected, they decompose more easily. The different behavior of the amides with

[1] This JOURNAL, **18**, 600. [2] Wallach: Ann. Chem. (Liebig), **184**, 1.
[3] *Ibid.*, **184**, 1; **214**, 193. [4] This JOURNAL, **17**, 99.

phosphorus pentachloride, therefore, does not depend on a difference of structure but on the properties of the amide chlorides.

If this view is correct, it must follow that if we increase the positive character of the molecule VI. by replacing radical R by an imido or anilido group, for example, we should obtain a compound capable of forming a comparatively stable amide chloride corresponding to formula V. This is precisely what takes place. Lengfeld and Stieglitz,[1] in their interesting work on the imidoethers of carbonic acid, have shown that carbodiphenylimide, $C_6H_5N=C=NC_6H_5$, not only unites with 1 molecule of hydrogen chloride, as stated by Weith, giving an imide chloride, formula VIII., but that this compound combines further with hydrogen chloride, and, as would be expected, a stable amide chloride results, which they call carbodiphenylimide dichloride, Formula IX.

$$C_6H_5NH-C{\Large\langle}\substack{NC_6H_5 \\ Cl}\,,\qquad\qquad C_6H_5NH-C{\Large\langle}\substack{NHC_6H_5 \\ Cl_2}\,.$$

<div align="center">VIII.   IX.</div>
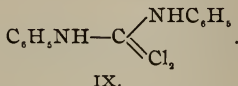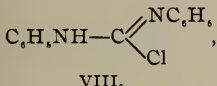
Lengfeld and Stieglitz state that this amide chloride melts at 130° and "is quite stable when kept from moisture and organic matter."

From the above it is evident that the results obtained by the action of phosphorus pentachloride on acet- and benzamides do not lead to the conclusion that these compounds have a hydroxyl group. Indeed, it is very improbable that the grouping $-N=\overset{|}{C}OH$ exists in any stable amide whatever.

Experimental Part.

α-Ketobenzmorpholine, $C_6H_4{\Large\langle}\substack{O-CH_2 \\ NH-CO}$.—This was prepared essentially according to Thate's method.[2] His directions for the purification of both orthonitrophenyloxyacetic acid and the anhydride, obtained by reduction, not being

suitable for the preparation of the material in large quanti-
ties, it was found better to proceed as follows :

After warming the mixture of orthonitrophenol, chloracetic
acid and alkali, and filtering, hydrochloric acid was added,
and the precipitate distilled in steam to remove unaltered
orthonitrophenol. The aqueous solution remaining deposits
the orthonitrophenyloxyacetic acid on cooling. For the re-
duction the acid was suspended in about 20 per cent. acetic
acid and iron filings slowly added. After the reduction, the
residue was boiled with alcohol and animal charcoal and the
anhydride crystallized from alcohol. The melting-point of
the material thus obtained is 169°, instead of 166° as given by
Thate. It may be crystallized conveniently from alcohol or
chloroform. In the latter solvent it is less soluble.

α-*Sodiumoxybenzparaoxazine*, $C_6H_4\begin{smallmatrix}O-CH_2\\ \\N=CONa\end{smallmatrix}$.— 0.8 gram

of sodium was dissolved in methyl alcohol and 5.0 grams of
α-ketobenzmorpholine were added. The solution was then
evaporated in a vacuum and the residue heated at 100° for
several hours, the pressure being kept at about 13 mm. The
perfectly dry mass then, on shaking, became granular, and a
sodium determination as carbonate gave :

	Calculated for $C_8H_7NO_2.CH_3.ONa$.	Calculated for $C_8H_6NO_2Na$.	Found.
Na	11.33	13.45	13.41

The material thus obtained did not dissolve in water, but
α-ketobenzmorpholine separated; on adding an excess of
alkali this readily dissolved. An attempt to prepare this
sodium salt by dissolving the keto compound in alcohol, add-
ing the calculated quantity of sodium ethylate, and then
ether, gave no precipitate.

n-Methyl-α-ketobenzmorpholine, $C_6H_4\begin{smallmatrix}O-CH_2\\ \\N-C=O\\ \\CH_3\end{smallmatrix}$. — This

compound was prepared by heating the dry sodium salt of
α-ketobenzmorpholine, suspended in benzene, to 135° for
several hours. It was found, however, that it is unnecessary

to prepare the dry salt as given above. It was more conveniently prepared as follows : 1.6 grams of sodium were dissolved in a small amount of methyl alcohol, 10 grams of α-ketobenzmorpholine were added, and then 20 grams of methyl iodide ; the whole was then heated to 135° for about seven hours. The contents of the tube were then filtered from sodium iodide, washed with ether, and distilled at 14 mm. pressure. After the alcohol and ether had evaporated, the material practically all boiled over at 156°. It readily solidified, and, on crystallizing from alcohol, large, stout, colorless prisms were obtained. These melted from 58°–59°, and a nitrogen determination gave :

	Calculated for $C_9H_9NO_2$.	Found.
N	8.58	8.58

It was found that this compound, like the following ethyl derivative, has little or no basic properties. It is insoluble in cold dilute hydrochloric acid. On warming, solution takes place, but, on cooling, the unaltered material separates in the form of needles or prisms. It dissolves more readily in concentrated hydrochloric acid, and is precipitated by water. Platinum chloride gave no precipitate when added to these solutions. A solution of the material in benzene gave no precipitate with dry hydrogen chloride. It is insoluble in alkali.

Orthomethylaminophenol, $C_6H_4$$\Big\langle{}^{OH}_{NHCH_3}$. — Not quite 2 grams of the above methyl derivative were heated with concentrated hydrochloric acid to 150°–160° for a number of hours. The hydrochloric acid was then evaporated on the water-bath and the residue treated with water, when it was found that the greater portion of the material had remained unaltered in this treatment ; the aqueous filtrate was treated with an excess of sodium carbonate, some sulphurous acid was added, and the whole shaken with ether. On evaporating the ether solution a small amount of almost colorless material separated in the form of plates. This was crystallized from petroleum ether when colorless thin spangles separated. On heating the pure material thus obtained, it began to darken

in color, rapidly at 80°, and decomposed, melting and turning black between 80° and 90°. Seidel,[1] who first obtained this compound, states that it crystallizes in plates that soon oxidize and take on a dark brown color. He says that, on heating, the material darkens and then melts above 80° with decomposition. The properties of the compound obtained by us agree perfectly with this description. We may add, as a further means of identifying this compound, that the hydrochloric acid solution gives a deep red-brown color with ferric chloride.

n-Ethyl-α-ketobenzmorpholine, $C_6H_4 \diagup\diagdown \begin{matrix} OCH_2 \\ | \\ CO \end{matrix}$ —This was

$N \diagdown C_2H_5$

prepared by means of sodium ethylate and ethyl iodide in the same manner as the above methyl derivative. The contents of the tube after the evaporation of the excess of ethyl iodide and alcohol all boiled over from 157°–159° at 15 mm. pressure. This material, unlike the methyl compound, was not obtained in the solid state. It had a light yellow color and a nitrogen determination gave:

	Calculated for $C_{10}H_{11}NO_2$.	Found.
N	7.91	8.20

This compound, like the corresponding methyl derivative, is not affected by acids or alkali under ordinary conditions. It dissolves in concentrated hydrochloric acid and is precipitated again by water. A slight warming is noticed on dissolving the material in concentrated sulphuric acid.

α-Silveroxybenzparaoxazine, $C_6H_4 \diagup\diagdown \begin{matrix} O - CH_2 \\ | \\ N = COAg \end{matrix}$ —This was

prepared by dissolving α-ketobenzmorpholine in alcohol and adding, first sodium ethylate (1 molecule) and then the calculated quantity of silver nitrate. The mixture, largely diluted with water, gave a white precipitate which, on stirring, became a light gray powder. This was filtered, washed with water, alcohol, and ether, and dried at a temperature

[1] J. prakt. Chem., **42**, 453.

somewhat below 100°. A silver determination gave the following :

	Calculated for $C_8H_6NO_2Ag$.	Found.
Ag	42.18	42.37

This salt is quite stable in respect to light. It is not readily decomposed by water or alcohol, although phenol immediately reduces it. The behavior of the silver salts of this compound and formanilide with phenols, is peculiar. Silver formanilide and silver 2-4-dichlorformanilide react with phenol with evolution of heat, the salts immediately blackening and regenerating unaltered formyl compound and silver. This is all the more remarkable, since silver 2-4-dichlorformanilide may stand mixed with water or alcohol for days without decomposition. Indeed, it can be boiled with water without any decomposition. Cold glycerin does not affect it, but phenol, largely diluted with benzene, an aqueous solution of hydroquinone, or an alcoholic solution of β-naphthol, almost immediately reduces the salt. A solution of thymol in benzene produces a mirror of silver, and resorcin in water slowly blackens the compound. From the above it is evident that these reactions involve an addition ; the addition-products being unstable then decompose into simpler molecules.

α-Methoxybenzparaoxazine, $C_6H_4 \begin{cases} O-CH_2 \\ | \\ N=COCH_3 \end{cases}$.—20 grams

of α-silver oxybenzparaoxazine and 20 grams of methyl iodide (1.5 molecules) were heated to 115°–120° for eight hours, the reaction then being practically complete. The material was then taken up in ether and filtered from the silver iodide.[1] The ether solution on evaporation in a vacuum over potash gave an oil which refused to solidify in a freezing-mixture. It was found to boil almost entirely between 135°–136° at 21 mm. pressure. The material thus obtained was a colorless oil with a pleasant odor, perhaps suggesting orange peel. A nitrogen determination gave :

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[1] It is advisable to shake the ether solution with alkali in order to remove unaltered orthoaminophenoxyacetic acid anhydride, which always accompanies the reaction product. Compare α-isoamyloxybenzparaoxazine.

	Calculated for $C_9H_9O_2N.$	Found.
N	8.58	8.66

On treating this oil with a drop of dilute hydrochloric acid it immediately solidified, giving crystals of α-ketobenzmorpholine. On exposure to air it slowly absorbs moisture, giving the same result. It is unaffected by cold alkali.

α-*Ethoxybenzparaoxazine*, $C_6H_4\!\!<\!\!\begin{array}{c}O-CH_2\\|\\N=COC_2H_5\end{array}$.—23 grams

of the above silver salt were heated with ethyl iodide (2 molecules) to 100°–130° for twenty hours. On extracting with ether and evaporating, an oil was obtained which deposited some unaltered α-ketobenzmorpholine. On distilling in a vacuum the oil boiled mostly between 135°–136° at 16 mm. pressure. It had a similar pleasant odor to that of the methoxy compound. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}O_2N.$	Found.
N	7.90	7.68

With acids this compound is immediately decomposed like the methoxy compound. It is unaffected by cold alkali.

α-*Isopropyloxybenzparaoxazine*, $C_6H_4\!\!<\!\!\begin{array}{c}O-CH_2\\|\\N=COC_3H_7\end{array}$. — 25

grams of the silver salt and 22 grams of isopropyl iodide were heated for nine hours at 120°–130°. On extracting them with ether, shaking the ether solution with dilute potassium hydroxide, and evaporating, an oil was obtained. This was distilled at 14 mm. pressure, when the greater portion boiled from 137°–138°. The material was colorless and had a peculiar odor, which, unlike the methyl and ethyl derivatives, was not pleasant. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}O_2N.$	Found.
N	7.32	7.31

It decomposes on standing, or with acids, giving α-ketobenzmorpholine.

α-*Isobutyloxybenzparaoxazine*, $C_6H_4\!\!<\!\!\begin{array}{c}O-CH_2\\|\\N=COC_4H_6\end{array}$.—25 grams

of the silver salt and 26 grams of isobutyliodide were heated for twenty-two hours at 120°–140°. The reaction-product, treated as above, gave an oil which was distilled at 21 mm. pressure, when it was found to boil practically from 160°–164°. It had a strong, somewhat disagreeable, odor. A nitrogen determination gave:

	Calculated for $C_{12}H_{15}O_2N$.	Found.
N	6.82	6.83

α-*Isoamylbenzparaoxazine*, $C_6H_4\begin{array}{c}O-CH_2\\|\\N=C-OC_5H_{11}\end{array}$. — 25

grams of the silver salt and 28 grams of isoamyl iodide were heated to 130°–150° for eighteen hours. On extracting with ether, an oil was obtained which gave no constant boiling-point, the solid anhydride distilling over with the oil. The distillate was taken up in ether and shaken with dilute potassium hydrate; the ether was evaporated and the oil then distilled at 174°–175° at 21 mm. pressure. It was colorless and had a disagreeable odor, somewhat resembling isoamyl oxalate. A nitrogen determination gave:

	Calculated for $C_{13}H_{17}O_2N$.	Found.
N	6.39	6.55

n-*Acetyl-α-ketobenzmorpholine*, $C_6H_4\begin{array}{c}OCH_2\\>CO\\N.COCH_3\end{array}$. — Acetyl

chloride reacts violently with dry α-silver oxybenzparaoxazine. For the preparation of this compound six grams of the silver salt were suspended in dry ether and the calculated amount of acetyl chloride was added. On filtering and evaporating, beautiful, long, white needles separated; these melted at 77°. A nitrogen determination gave:

	Calculated for $C_{10}H_9O_3N$.	Found.
N	7.32	7.43

This acyl compound is quite stable. It can be crystallized unaltered from water.

n-*Benzoyl-α-ketobenzmorpholine*, $C_6H_4\begin{array}{c}O-CH_2\\>CO\\N-COC_6H_5\end{array}$. —

Six grams of the silver salt were suspended in benzene and benzoyl chloride added. From the benzene solution beautiful, colorless, compact prisms separated. These melted at 93°, and a nitrogen determination gave :

	Calculated for $C_{16}H_{11}O_3N$.	Found.
N	5.53	5.46

This compound can be crystallized from water.

α-Phenylaminobenzparaoxazine, $C_6H_4 \Big\langle \begin{matrix} O-CH_2 \\ | \\ N=C-NHC_6H_5 \end{matrix}$.—

When α-ethoxybenzparaoxazine and aniline were mixed, in molecular proportions, the mixture solidified after standing twenty-four hours to a white, crystalline mass. It is readily soluble in alcohol from which it crystallizes in colorless, compact prisms melting at 126°. A nitrogen determination was made with the following result :

	Calculated for $C_{14}H_{12}N_2O$.	Found.
N	12.50	12.53

The *hydrochloride* prepared by dissolving the above cyclo-amidine in aqueous hydrogen chloride separated in the form of colorless, four-sided prisms, which melt with decomposition from 220°–223°.

The *hydroiodide*, $C_{14}H_{12}N_2O \cdot HI$, crystallizes from water in colorless plates, which melt from 195°–196°. An iodine determination gave :

	Calculated for $C_{14}H_{13}N_2OI$.	Found.
I	36.26	35.77

The *nitrate* separates from dilute nitric acid in the form of colorless four- and eight-sided plates, melting at 147°.

α-Metachlorphenylaminobenzparaoxazine,

$C_6H_4 \Big\langle \begin{matrix} O-CH_2 \\ | \\ N=C-NC_6H_4Cl \end{matrix}$.—A mixture of α-ethoxybenzpara-

oxazine and 1 molecular preparation of metachloraniline did not solidify after standing a week. The material was then taken up in dilute hydrochloric acid, and, after filtering, the amidine was precipitated with ammonia. It was then ob-

tained in the solid condition and, on crystallizing from benzene, it separated in the form of colorless plates and melted at 112°–114°.

	Calculated for $C_{14}H_{11}N_2O.Cl.$	Found.
N	10.83	10.06

The *hydrochloride*, $C_{14}H_{10}N_2OCl.HCl$, crystallized from alcohol, melts with decomposition at 205°–207°.

α,β-Naphthylaminobenzparaoxazine,

$$C_6H_4\left\langle\begin{array}{c}O-CH_2\\ |\\ N=C-NHC_{10}H_7\end{array}\right.$$. — 2.4 grams of *α*-isopropyl benzparaoxazine and 2 grams of *β*-naphthylamine were heated in alcohol for eighteen hours on the steam-bath. On evaporating off the alcohol and crystallizing the residue from benzene, white leaflets separated which melted from 154°–155°.

	Calculated for $C_{18}H_{14}N_2O.$	Found.
N	10.22	10.00

α-Isobutylaminobenzparaoxazine,

$$C_6H_4\left\langle\begin{array}{c}O-CH_2\\ |\\ N=C-NHC_4H_9\end{array}\right.$$. — This was obtained by mixing *α*-ethoxybenzparaoxazine with isobutylamine. It forms a thick varnish at ordinary temperature, which, only after long standing, showed evidence of crystallization.

The *hydrochloride* may be crystallized from water or chloroform. From the latter it separates in the form of flakes, melting from 220°–223°.

	Calculated for $C_{12}H_{17}N_2OCl.$	Found.
Cl	14.76	14.40

α-Allylaminobenzparaoxazine, $C_6H_4\left\langle\begin{array}{c}O-CH_2\\ |\\ N=C-NHC_3H_5\end{array}\right.$.—
The mixture in this case did not solidify on long standing. It was taken up in benzene and the hydrochloride precipitated by means of dry hydrogen chloride. This precipitate was crystallized from benzene containing some alcohol, when colorless needles, melting at 190°, were obtained. These

were dissolved in alcohol. From the solution ammonia pre-cipitated an oil which soon solidified. This was crystallized from ligroïn with a little benzene, when the material separa-ted in colorless prisms melting at 63°.

The *hydrochloride* is readily soluble in water and alcohol; it was analyzed with the following result:

	Calculated for $C_{11}H_{12}N_2OCl$.	Found.
Cl	15.8	15.9

New Haven, May, 1898.

LXII.—THE ACTION OF AMINES ON ACYLIMIDO-ESTERS: ACYL AMIDINES.

By H. L. Wheeler and P. T. Walden.

In a previous paper we described a series of acylimido-esters, and stated that they react with ammonia and bases giving acylamidines. We are now prepared to describe some of these amidines and to discuss their formation.

Few acylamidines have hitherto been described. The ac-tion of acyl chlorides and anhydrides on the free amidines does not always lead to the formation of acyl deriva-tives.[1] Pinner obtained benzoylbenzamidine from benzami-dine and benzoic acid anhydride, and also from benzonitrile by condensation with sulphuric acid. On account of the ease with which this compound separates ammonia, giving dibenzamide, he assigned the structure represented by For-mula I. to this substance.

We have found that the benzoylbenzimido esters, *i. e.*,

$$C_6H_5C\overset{\diagup NCOC_6H_5}{\diagdown OR}$$ react with ammonia, giving a compound

in every respect identical with that obtained from benzonitrile by the method of Pinner, while an isomeric compound, Formula II., would be expected, if the reaction takes place, as is usually assumed, by double decomposition, replacement or substitution.

[1] Pinner: Die Imidoäther und ihre Derivate.

$$C_6H_5C\diagup^{NHCOC_6H_5}_{\diagdown NH} \qquad C_6H_5C\diagup^{NCOC_6H_5}_{\diagdown NH_2}$$

I.   II.

The action of amines on the acylimido esters, like the action of amines on the amidines themselves, does not take place by direct replacement, but involves the intermediate formation of an unstable addition-product :

$$C_6H_5C\diagup^{NCOR}_{\diagdown OR} + H_2NH = C_6H_5C\overset{NHCOR}{\underset{NH_2}{-}}OR$$

III.

This hypothetical addition-product can then separate alcohol in two ways, giving an acyl amidine corresponding to either of the above forms.

It cannot be maintained that, because benzoylbenzamidine easily decomposes into dibenzamide and ammonia, its structure is to be represented by Formula I., since in this decomposition hydrolysis takes place with addition of water, forming a product similar to III., and the same addition-product must result from I. and II.

That this view is correct and that this decomposition has no significance in regard to the structure of the acyl amidines, is shown by the behavior of the analogously constituted acylimido esters, *i. e.*, benzoylbenzimidoethyl ester and benzoylphenylacetimidoethyl ester. These compounds easily decompose with water, under the same conditions as benzoylbenzamidine, as follows :

$$C_6H_5C\diagup^{NCOC_6H_5}_{\diagdown OC_2H_5} \;\longrightarrow\; C_6H_5C\overset{NHCOC_6H_5}{\underset{OC_2H_5}{-}}O\,H$$

$$C_6H_5CH_2C\diagup^{NCOC_6H_5}_{\diagdown OC_2H_5} \;\longrightarrow\; C_6H_5CH_2C\overset{NHCOC_6H_5}{\underset{OC_2H_5}{-}}O\,H$$

That is, the first gives dibenzamide and alcohol, while the second gives benzamide and ethylphenyl acetate. In other words, the first apparently decomposes at a single bond; the second at the double bond. Here are then two compounds, not only of the same structure, but also similar to the acyl amidines, which decompose or are hydrolyzed in two different ways.

The structure of these amidines cannot therefore be determined by their decomposition-products, and further work will be required before this question is settled.

Beckmann and Sandal,[1] in their interesting work on the rearrangement of α-benzilmonoxime, have recently obtained benzoylbenzimidechloride, $C_6H_5C{\begin{smallmatrix} NCOC_6H_5 \\ \\ Cl \end{smallmatrix}}$, a compound which shows, as would be expected, many properties in common with the acylimido esters. It readily decomposes into dibenzamide and unites with primary bases giving acyl amidines. With ammonia it gives the acyl amidine described by Pinner and with aniline an acyl amidine identical with that obtained by us from the benzoylbenzimido esters. Beckmann and Sandal, however, did not succeed in preparing acyl amidines from this compound and secondary amines, and here it may be stated that we have repeatedly made attempts to prepare acyl amidines from secondary bases and various acylimido esters, but in each case also without success.

In support of Pinner's formula for benzoylbenzamidine, Beckmann and Sandal state that benzaldehyde does not combine with this substance, and that with benzenesulphochloride it gives a compound insoluble in alkali.

The acyl amidines, described below, are stable towards cold alkali. Some of them dissolve in acids and may be precipitated unaltered by alkali or ammonia. They combine with one equivalent of hydrogen chloride to form salts which are comparatively unstable. In aqueous solution these salts soon decompose as follows :

[1] Ann. Chem. (Liebig), **296,** 279.

$$C_6H_5C \overset{\displaystyle NHCOR}{\underset{\displaystyle NHC_6H_5}{\diagup}} \!\!\!-Cl \quad + H_2O = \quad \begin{matrix} C_6H_5CO.NHCO.R \\ + \\ C_6H_5NH_2.HCl \end{matrix}$$
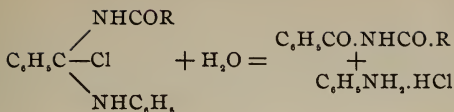
The diacylamide generally separates pure and in the form of a glistening mass of colorless crystals.

Experimental Part.

Benzoylbenzamidine.—This was formed when 10 grams of benzoylbenzimidonormalpropyl ester were warmed in alcoholic solution with the addition of aqueous ammonia in excess. On diluting the alcoholic solution, in which it is readily soluble, this compound separated as an oil which readily solidifies. It was purified by dissolving or crystallizing it from a mixture of ligroïn and alcohol. It melted constantly at 100°. Pinner[1] gives the melting-point of this compound as 106°. Gumpert[2] states that it melts at 105.5°, and Beckmann and Sandal give 98° as its melting-point. In addition to the above we have prepared this compound from benzoylbenzimidoethyl ester and ammonia. This product also melted at 100°. A nitrogen determination in the sample prepared as first stated gave:

	Calculated for $C_{14}H_{12}N_2O$.	Found.
N	12.50	12.53

In order to determine whether this compound is identical with that obtained by Pinner, we have prepared the substance by dissolving benzonitrile in fuming sulphuric acid, according to his directions, and have found that the compound thus obtained also melted sharply at 100° to 101°. A crystallographic examination of the two products was made by Mr. C. H. Warren, to whom the authors wish to express their thanks for the following report: "A trial on the reflection goniometer showed that the faces gave poor reflections, consisting of a number of faint signals for each face, and that a full description was not practicable. However, enough measurements were made of the same zone on both lots of crystals to show satisfactorily the identity of the two specimens. The crystals

[1] *Loc. cit.*   [2] J. prakt. Chem., **30**, 90.

show monoclinic symmetry. The forms observed were *c* 101 (?), *y* 10$\bar{1}$ (?), and *m* 110, probably. On many of the crystals the edges between the prism and top faces were highly modified. The measurements of zone *c*$\wedge$*y* were as follows:

	Ours.			Pinner's.	
c$\wedge$*y*	49°	9′		49°	10′
y$\wedge$*c*′	130°	51′		130°	40′

The angles measured agree closely considering the poor quality of the reflections." The crystallographic and chemical properties therefore show that the two products are identical. On warming the hydrochloric acid solutions, both products give dibenzamide.

Benzoylbenzamidine hydrochloride, $C_6H_5C\begin{smallmatrix} \diagup NHCOC_6H_5 \\ \diagdown NH_2 \end{smallmatrix}Cl$.—
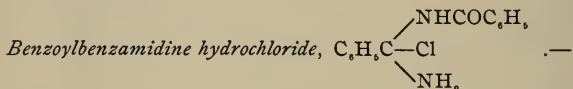
The above amidine was dissolved in benzene containing some chloroform, and the solution was saturated with hydrogen chloride, when a heavy, thick oil separated. This oil consists probably of a dihydrochloride. It is very unstable. The material was protected from moisture and dry carbon dioxide was led in, to expel the excess of hydrogen chloride. After a number of hours the material crystallized in small colorless prisms. On pressing on paper it was found to be somewhat sticky. It was then heated to 50° when considerable hydrogen chloride escaped, and the mass became a sandy powder. Thus obtained it melted, not sharply, at about 190°, and a chlorine determination gave the following:

	Calculated for $C_{14}H_{13}N_2O.Cl$.	Found.
Cl	13.6	12.9

This salt is readily soluble in water, and decomposes with the separation of dibenzamide.

The *platinum chloride double salt* was obtained by dissolving the amidine in aqueous hydrochloric acid and adding platinum chloride. It separates as a straw-yellow precipitate which darkens on heating at about 225° to 230°, and melts at 240°. A platinum determination gave:

	Calculated for $(C_{14}H_{12}N_2O.HCl)_2PtCl_4$.	Found.
Pt	22.7	22.5

Benzoylethylbenzamidine.—This was prepared by allowing six grams of benzoylbenzimidonormalpropyl ester to stand in alcohol for some time mixed with an excess of a 33 per cent. solution of ethylamine. The alcohol was then evaporated, and it was attempted to crystallize the residue from dilute alcohol, ligroïn, and benzene, but a sharp melting-point was not obtained until the material was dissolved in dilute hydrochloric acid, precipitated by ammonia, and then crystallized from strong alcohol. Thus obtained it separated in beautiful colorless prisms which melted at about 87° to 88°. This compound is undoubtedly identical with the compound obtained by Lossen[1] by acting on ethyl benzamidine with benzoyl chloride. He gives the melting-point as 88°.

Benzoylphenylbenzamidine.—4 grams of benzoylbenzimidoethyl ester were mixed in ether with 1.5 grams of aniline. No evidence of any reaction was noticed after standing over night. The ether was then evaporated, and the residue heated on the steam-bath, when it solidified. The material was found to crystallize beautifully from alcohol, in thick bunches of rhombohedrons apparently. The material is insoluble in cold dilute sodium hydrate and melts at 143°. This gave on analysis :

	Calculated for $C_{20}H_{16}N_2O$.	Found.
N	9.33	9.32

This compound has recently been obtained by Beckmann and Sandal.[2] They find that the compound melts at precisely the same temperature as we do.

When dry hydrogen chloride was passed into a chloroform solution of this acyl amidine, no precipitate resulted. On evaporating the chloroform in a stream of dry carbon dioxide, an amber-yellow varnish remained. When warmed with water this gave a mass of colorless needles or prisms, which melted at 149°, and had all the properties of dibenzamide.

An attempt was made to prepare *benzoylmethylphenylbenz-*

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[1] Ann. Chem. (Liebig), **265**, 162.   [2] *Loc. cit.*

amidine by acting on benzoylbenzimidoethyl ester with mono-
methylaniline, when it was found that this secondary aniline
did not give an acyl amidine. 4 grams of the acylimido ester
and 1.7 grams of methylaniline were heated to 100°, then for
some time kept at about 70°, and, finally, after long standing,
crystals separated. These crystallized from alcohol in prisms
melting at 147°–148°. A nitrogen determination gave :

	Calculated for acylanidine.	Calculated for dibenzamide.	Found.
N	8.91	6.22	6.17

With ethylaniline the same result was obtained. The
above analyzed material was soluble in alkali and precipitated
again by acids; it was therefore dibenzamide.

Acetylphenylbenzamidine.—When acetylbenzimidoethyl es-
ter is mixed with aniline and allowed to stand, the mixture
solidifies. On crystallizing from 95 per cent. alcohol, it
forms stout, colorless crystals, which melt at 138°.5. A nitro-
gen determination gave :

	Calculated for $C_{15}H_{14}N_2O$.	Found.
N	11.76	11.94

Acetylparatolylbenzamidine.—*p*-Toluidine and acetylbenz-
imidoethyl ester were mixed in molecular proportions and
allowed to stand, when the mixture soon solidified. The
material was crystallized from 50 per cent. alcohol, when it
was found to melt at 136°.5. A nitrogen determination gave :

	Calculated for $C_{16}H_{16}N_2O$.	Found.	
		I.	II.
N	11.11	11.30	11.30

Acetylmetachlorphenylbenzamidine.—1.5 grams of acetylbenz-
imidoethyl ester and 1 gram of metachloraniline on mix-
ing solidify after some time. The material crystallized from
alcohol separates in clusters of colorless needles or prisms. It
melts at 128°–129°. A nitrogen determination gave :

	Calculated for $C_{15}H_{13}N_2OCl$.	Found.
N	10.27	10.08

A portion of the analyzed material was dissolved in dry
benzene, and the solution was saturated with hydrogen chlo-

ride, when a sticky precipitate separated. The excess of hydrogen chloride was expelled by means of a current of dry carbon dioxide. The precipitate, unsuitable for analysis, dissolved readily in water, and, on warming up to 80°, colorless needles separated. These melted from 118°–119°, (acetbenzamide), and dissolved readily in dilute sodium hydroxide. The solution on standing deposited plates (benzamide).

2,4-Xylylbenzamidine.—When 2,4-xylidine and acetylbenzimidoethyl ester were mixed and allowed to stand a long time, a solid separated. The material was too soluble to crystallize from alcohol. The alcoholic solution was precipitated with dilute potassium hydrate, in order to remove any acetbenzamide, when an oil separated. This, on standing, solidified to a mass of prisms. The material was readily soluble in warm ligroïn, and crystallized in long, colorless needles, melting at 106°. Nitrogen determinations showed that this is not the expected acetyl-2,4-xylylbenzamidine, but that the acetyl group had been removed.

	Calculated for acylamidine $C_{17}H_{18}N_2O.$	Calculated for amidine $C_{15}H_{16}N_2.$	Found.	
			I.	II.
N	10.52	12.50	12.34	12.36

The material dissolved readily in dilute hydrochloric acid and gives a yellow precipitate with platinum chloride.

Acetyl-β-naphthylbenzamidine was formed when β-naphthylamine was warmed with acetylbenzimidoethyl ester. The product was crystallized from 95 per cent. alcohol, when it melted at 137°. A nitrogen determination gave:

| | Calculated for $C_{19}H_{16}N_2O.$ | Found. |
| N | 9.72 | 9.64 |

Propionylphenylbenzamidine.—When propionylbenzimidoethyl ester was mixed with aniline, the mixture solidified in about four or five hours. It was crystallized from alcohol, when small, stout prisms of a yellowish-white color were obtained. These melt at 138°, and a nitrogen determination gave:

| | Calculated for $C_{16}H_{16}N_2O.$ | Found. |
| N | 11.11 | 11.01 |

Dry hydrogen chloride led into a benzene solution of this acylamidine gave a sticky precipitate. It was dissolved in water, and in a few minutes a mass of colorless prisms separated. These melted at 98°, and are propionylbenzamidine, which compound we described in a previous paper. On warming this with aqueous ammonia, the material dissolved, and, on cooling, plates of benzamide separated, melting at 128°.

An attempt was made to prepare *normalbutyrylbenzamidine* by dissolving the butyrylbenzimidoethyl ester in dilute alcoholic ammonia in the same manner as benzoylbenzamidine was obtained. The product obtained, crystallized from water, melted at 126°–127°, and a nitrogen determination gave :

	Calculated for butyrylbenzamidine.	Calculated for benzamide.	Found. I.	II.
N	14.7	11.57	11.71	11.74

The material thus obtained had all the properties of benzamide. It was found later that acetylbenzimido and propionylbenzimido esters by a similar treatment also give benzamide.

Normalbutyrylphenylbenzamidine. — Butyrylbenzimidoethyl ester reacts with aniline on warming, and the solid thus obtained on crystallizing from absolute alcohol separated in the form of colorless prisms and melted at 137°. A nitrogen determination gave :

	Calculated for $C_{17}H_{18}N_2O$.	Found.
N	10.52	10.53

An attempt to prepare *normalbutyrylmetanitrophenylbenzamidine*, by warming metanitraniline and butyrylbenzimidoethyl ester in molecular proportions, resulted in the formation of a yellow varnish, which has stood for months without depositing crystals. Acetylbenzimidoethyl ester combines with isobutyl amine, and propionylbenzimidoethyl ester combines with allyl amine. Heat is evolved in both cases. The products formed are oils which have not been further investigated.

New Haven, May, 1898.

LXV.—ON A NEW FORM OF WATER BLAST.

By Bertram B. Boltwood.

Various forms of apparatus have been devised for supplying compressed air to blast-lamps, small gas furnaces, etc., where relatively small volumes of air at low pressures are required. Of those forms which make use of the action of a small jet of water, one designed by Richards, and another described by Muenke, have found the widest application. Both of these appliances operate on the injector principle. A small jet of water is projected through the narrow orifice of a tube of gradually increasing diameter. The jet of water sweeps with it a considerable volume of air, which, together with the water, passes into a receiver, where the two are separated. The efficiency of this action is increased by the introduction of a projecting step in the injector tube, or by giving the form of an undulating curve to the tube itself. This deflects the jet, diminishing its velocity and causing it to completely fill the tube.

The effectiveness of this form of apparatus is, however, limited. This follows as a necessary result of the system upon which it is constructed. The orifice through which the jet passes must, of course, have a greater cross-section than the jet itself, for otherwise no air would be drawn through it. If the size of the orifice be increased beyond this, the efficiency reaches a certain maximum, beyond which any further increase in the size of the orifice causes a reduction in both the pressure and the volume of the air supplied. With the maximum free space, which must necessarily be small, for the admission of air, about the circumference of the jet, the friction experienced by the air in passing must be very considerable.

In the blast which is here described the objectionable features mentioned above have been done away with, and as a result the efficiency of the apparatus has been greatly increased.

The essential parts of the apparatus are the following : The receiver A, having the form of a cylinder 8 inches in height and 6 inches in diameter, divided into three compartments, b, c, and d, by the partitions p and p', there being a

circular opening 2 inches in diameter between b and c, and two smaller openings between c and d (as shown in Fig. I.); the injector tube l, $7\frac{1}{2}$ inches long and $\frac{5}{8}$ inch outside diameter, provided at the top with the small funnel-shaped projection g; the outlet tube f, having a diameter equal to that of l, extending upward from c and curving over and downward

Fig.I.　　Fig.III.
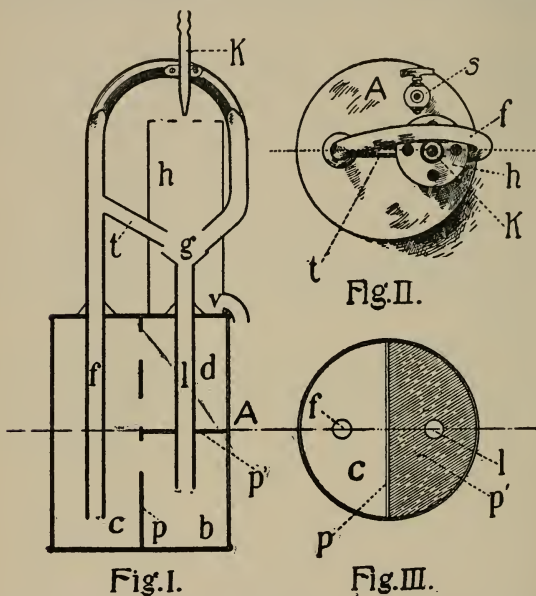
to g; the tube t ($\frac{7}{16}$ inch in diameter) opening into f and extending to g; the stop-cock s opening into d; and the nozzle k, having an orifice $\frac{1}{16}$ inch in diameter, attached to the upper part of the tube f. The upper part of the tube f is bent slightly out of the plane of section in order that the axis of k and l may *exactly* coincide.

The action of the blast is as follows: The cock s is opened and the water is turned on. The jet of water issuing from k passes through l and falls into the compartment b. When

the level of the water in *b* rises above the lower end of the tube *l* a considerable volume of air is swept into *A*. This air escapes through *f* and *s* and later through *s* only. The water flows from *b* into *c* through the opening in the partition between them. The cock *s* is now closed and the increase of pressure in the receiver causes the water to be forced up through *f* and into *g*. The jet from *k* now strikes upon the surfaces of the water in *g* and sweeping with it a large volume of air, drives it downward into *A*. If the cock *s* be now opened, a stream of air of a volume and pressure sufficient to supply a large blast-lamp will be obtained.

The manipulation of the apparatus in practice is extremely simple. The proper adjustment of *s* for giving the maximum efficiency is readily determined. A glass water-gauge attached to the outside of *A*, and connected with the compartment *c*, is very convenient, but not at all necessary. Spattering is prevented by surrounding *g* with a cylindrical case *h*, having openings in the top to allow the entrance of air, and an overflow pipe *v*, for the escape of the water. When the blast is set up in a permanent position it is best to place it well below the level of the blast-lamp bench, and to make the connection between the compartment *d* and the stop-cock *s* by means of a pipe at least 1 inch in diameter. This will prevent any water from reaching the lamp, in case *s* is not properly adjusted. When *s* is attached directly to the receiver, as shown in Fig. II., a good-sized bottle inserted between *s* and the lamp will serve the same purpose.

Fig. I. is a vertical section of the complete apparatus; Fig. II. is a projection from directly above; and Fig. III. is a section through the middle of the receiver.

The advantages of this form of blast are: That the orifice offered for the entrance of water and air is of such ample size that any considerable friction is avoided; that the injector tube is perfectly straight and free from any obstruction, so that the jet of water is not deflected and the maximum effect is obtained; and that the energy of the jet is transmitted to a much greater volume of water, which circulates continuously through the apparatus, flowing from *f* through *l* and acting as a piston which completely fills the cross-section of the tube.

Two points of construction are absolutely essential to the satisfactory working of the blast. The shape of the nozzle k must be such that the jet of water igniting from it is perfectly cylindrical and unbroken for at least 15 inches of its length, and the jet must pass *exactly* through the longitudinal axis of the tube l. The latter requirement is most easily assured by leaving the attachment of the bottom of the receiver until the last, and setting the nozzle so that the jet falls in the proper position.

A number of tests were carried out in order to determine the efficiency of the blast described in this article as compared with that of the blasts of Richards and Muenke. The volume of water consumed and the volume of air furnished was measured in each case. The results are given in the following table :

	Volume of water consumed per minute. Liters.	Volume of air supplied per minute. Liters.	Ratio.
Muenke,	5.1	5.5	1.1
Richards,	6.6	7.2	1.1
New form,	2.7	8.1	3.0

The pressure of the water used was the same in each case and was not more than 100 feet. The air was measured at atmospheric pressure.

This new blast can be obtained from Messrs. Eimer and Amend, of New York City, who have been authorized to carry out its manufacture.

NEW HAVEN, CONN., May, 1898.

LXIV.—ON THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.
PART I.

By James Locke.

The problems set before the inorganic chemist by the periodic system, which have directly or indirectly guided almost all the inorganic investigations of the past thirty years, may be divided, roughly in the abstract but very sharply in the results obtained, into two classes. The one, of the fruitfulness of which no one can complain, deals with the superficial group-relations which exist between the members of the various families. Their solution leads to what may be called the development of group analogies. The problems of the second class, on the other hand, have either been entirely neglected, or their study has yielded only the most unsatisfactory results. These have had to do with the contradictions of fact which the system, as formulated by Mendeléeff, involved, and to which the system should in course of time adapt itself. But all the more important inconsistencies which it presented in the year 1870 still remain, and are finally recognized as facts which, for the sake of a convenient principle, must not be forced into a conspicuous position. The behavior of the elements of low atomic weight; the appearance of one and the same element in more than one degree of oxidation; the properties of the platinum metals; either receive no expression in the system, or they stand in direct contradiction to its laws. The difficulties involved, however, are confined chiefly to the compounds. The relations between the elements, *as elements*, are in almost every case clearly pointed out in the usual tables. This is true in regard to both the physical and chemical properties of the elements themselves. In this paper, therefore, only that part of Mendeléeff's law will be discussed, which says that the *nature of the compounds of an element is also a function of its atomic weight*.

Of the 65 elements having places in the system, 9 of them, iron, cobalt, nickel, and the platinum metals, are put in a

vertical row by themselves, where they form the so-called 8th family, a family which may be said to fall outside the system proper. In this group many of the regularities which can be traced through other families are wanting.

The valency of the elements increases by one in each successive vertical row of the system, until the fourth is reached, after which each family yields two series of compounds, the one of increased, the other of decreased valency. In the potassium-nickel series, for instance, the various elements should enter into compounds with the valencies :

$$K^I, Ca^{II}, Sc^{III}, Ti^{IV}, V^V, Cr^{VI}, Mn^{VII}, (Fe, Co, Ni)^{VIII}.$$
$$V^{III}, Cr^{II}, Mn^I.$$
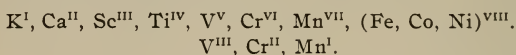
So, since chromium falls within the 6th family, the greatest weight is laid upon the fact that chromic acid and its salts show such close analogy to sulphuric acid and the sulphates. The fact that potassium permanganate is isomorphous with the perchlorate, and like the latter only sparingly soluble in cold water, likewise assumes the utmost importance. If compounds of iron, cobalt, and nickel were known, in which these elements were octavalent, they, too, would possess the greatest theoretical value. But, with the exception of nickel carbonyl, a doubtful case of octavalency, these theoretically necessary compounds have never been obtained. Up to the present no one has succeeded in getting beyond the ferric acid of hexavalent iron.

That the decrease in valency, on the other hand, must stop before the 8th family is reached, is obvious, for the 7th family is itself univalent, and a further decrease would prevent iron, cobalt, and nickel from forming any compounds at all. But this regularity ceases still further on,—with chromium. No univalent manganese compounds have been obtained. Now, inasmuch as the iron, cobalt, and nickel compounds fail to conform with a regularity which can otherwise be traced throughout the entire sytem, they are assigned an entirely different rôle from that of other elements. They form transition stages, so to speak, from the manganous salts to the copper compounds of the next horizontal row. But this transition is not from the compounds of univalent man-

ganese to those of univalent copper. Univalent manganese is unknown. It is from divalent manganese to divalent copper—to copper in a degree of oxidation which in no way corresponds to the position of this element in the system, and the salts of which have nothing more in common with the cuprous compounds, than has sulphuric acid with hydrogen sulphide ; the same element can be obtained from both, and even then the road is by no means a smooth one, for directly before manganese stands chromium, and since divalent manganese has no place in the system, the chromous salts must be regarded as the true starting-point for the transition. But the transition from the unstable divalent and stable trivalent derivatives of chromium to those of ferrous and ferric iron is through a manganese in which the relative stability in the two degrees of oxidation is exactly the reverse.

I know I lay myself open here to the charge of expecting too much from the system. But why? Here is a great law of nature, the correctness of which no one can doubt. But in order to illustrate this law, an empirical arrangement of the elements is formed, and this arrangement we are all too apt to confuse with the law itself. The periodic system is satisfactory enough for the elements. Lothar Meyer's curves of the atomic volumes and melting-points prove this. For the compounds it is *unsatisfactory*. And in order to find out how the law does apply to compounds, we must sift out and discuss the discrepancies which the system shows in regard to them.

As with iron, cobalt, and nickel, so it is with all the other members of the 8th group. These metals, at the time of the promulgation of the periodic system, were assigned a position which, satisfactory though it was in illustration of their properties as elements, was in regard to their compounds absolutely abnormal ; and no amount of investigation and speculation, with the periodic system as a basis, can clear up the contradictions which their position entails.

A second point upon which no light has been thrown lies in the behavior of the so-called "typical elements." These, as Ostwald remarks, instead of being types of the families at the head of which they stand, have in the majority of cases

properties directly at variance with those of the other members of their respective groups. In his "Principles of Chemistry" Mendeléeff says : "The elements of the first two series have the least atomic weights, and in consequence of this very circumstance, although they bear the general properties of a group, still they show many peculiar and independent properties. These lightest elements are :

> H ;
> Li, Be, B, C, N, O, F ;
> Na, Mg, ··, ··, ··· ''

As Mendeléeff left these elements, "typical," so they have remained, and the history of thirty years contains no mention of a successful attempt to unite them more closely than by that ill-fitting word to the groups to which they should show analogies.

Lithium is the lightest of all the elements having places in the system. It should, therefore, from the above, have the greatest number of independent properties of any of the typical elements. Or, one should at least expect to find metallic lithium and lithium compounds varying from the higher alkali metals and their derivatives in one and the same degree, since their departure from the rest of the group is conditioned by one and the same cause. The abnormal behavior of the other typical elements should be along the same lines as in the case of lithium and its compounds. The essential properties of metallic lithium stand in strictest analogy to those of the other alkali metals. Metallic beryllium fits in accurately in the series formed by magnesium, zinc, cadmium, and mercury. Between boron and aluminium the analogy is less clear ; but it appears again in full force in the properties of free carbon and silicon. The two elements show in their physical properties, allotropic modifications, and indifference to reagents, the strongest similarity. Fluorine and chlorine, in the elementary state, present the most striking analogies ; and the gradations in character which the free halogens undergo with increasing atomic weight, from fluorine through to iodine, yield one of the most perfect chemical series imaginable.

Of the 7 elements making up the first horizontal row, therefore, at least 4 possess, *in the elementary state*, properties closely akin to those of the subsequent elements in their respective families, and complete the series which the latter form.

Now, if the periodic system is true for compounds as well as for the elements themselves, then the compounds of analogous elements must be analogous—a simple deduction from the law which is not altered in its bearing, by the fact that the elements with which we happen to be dealing fall within the so-called typical class. If the low atomic weights, therefore, of the four elements, lithium, beryllium, carbon, and fluorine, are not of such influence as to prevent their ranking as they should, in their respective families, we must expect that their compounds will also show analogy to those of the other members of their groups. The compounds of lithium vary more or less from those of the other alkali metals, it is true ; its phosphate and carbonate, especially, are less soluble ; but, nevertheless, the lithium salts in general possess the characteristics of alkali derivatives, to an extent which would certainly prevent anyone from considering lithium as anything but an alkali metal. Carbon and silicon likewise bear close relationship in their compounds. The property of carbon which gives rise to organic radicals and the existence of such a multitude of combinations between but a few elements, the ability of the carbon atoms to unite with one another, likewise appears in silicon. The silicon hydrides, the various chlorides, bromides and iodides, silicon-chloroform, and the complex oxygen compounds, such as silico-oxalic and mesoxalic acids, illustrate fully the strong similarity between the influence of tetravalent carbon and that of silicon upon their compounds.

The law, and its expression by the periodic system, therefore, holds good in the case of lithium and carbon, and no fault can be found with the typical behavior of the two elements. Now, if the effect of small atomic weight upon both lithium and carbon, is too slight to cause in the nature of their compounds any great variation from that of their homologues, one has a perfect right to assume that this separating influence will not be greater in an element which, in

its atomic weight, lies between the two ; but, after a comparison, unprejudiced by the fact that an analogy between the compounds of beryllium and magnesium is required by their positions in the system, can a single trace of true resemblance be found between them, or between beryllium derivatives and those of any other element in the second vertical row ? Magnesium hydroxide and beryllium hydroxide are both dibasic, it is true.   But there the similarity ceases.

A strongly distinctive feature of all magnesium, zinc, and cadmium salts is seen in their behavior toward ammonia and ammonium salts.   They also have a pronounced tendency to form double salts with the compounds of other metals. Their oxides are insoluble in water, but soluble even in weak acids.   Calcium, strontium, and barium, on the other hand, are characterized by their soluble, strongly alkaline hydroxides, by their difficultly soluble sulphates, and by the difficulty with which they enter into double salts.   These are group characteristics, the presence of any one of which indicates the others.   They give a tone to, and define the nature of, all the compounds of the two series.   But to beryllium salts not one of them applies.   Similar to magnesium though the metal be, its compounds show perfect indifference to ammonium salts; they form no double salts,[1] and the oxide is practically insoluble even in strong, hot acids ; as little soluble, in fact, as alumina.   This last fact, together with the ready solubility of the sulphate and of the fluoride, and the insolubility of the sulphide, etc., prevent any comparison of the beryllium compounds with those of the alkaline earths.

With fluorine, the nature of the compounds of which it will be unnecessary to discuss in full, the case is similar, although its atomic weight is nearly three times as great as that of lithium.   The properties of the free element show it to be a pronounced halogen, with characteristics which one would expect to find in a halogen of lower atomic weight than chlorine.   But its compounds are not only widely different from

[1] Certain double fluorides must be noted as exceptions to this statement. The double sulphates, phosphates, etc., known, may be disregarded, as they can be represented by simple constitutional formulas, and this formation is of less significance than that of double halogenides, and the like. Both calcium and strontium yield double sulphates.

those of chlorine, but they often vary in a direction contrary to that of the gradations observed in the rest of the series. Fluorine, it is true, forms in common with the other halogens an acid of the type HR. But in distinction from hydrochloric, hydrobromic, and hydriodic acid, hydrofluoric acid has a remarkably low molecular conductivity ; and its salts, in the majority of cases, have properties which are directly the opposite of those of the chlorides, bromides, and iodides. The most pronounced chemical characteristic of the halogen acids certainly lies in the solubility of their salts with heavy metals, and the insolubility of the silver, cuprous, and mercurous compounds. The *fluorides* of silver and mercury, on the other hand, are readily soluble : those of calcium, strontium, barium, magnesium, manganese, iron, cobalt, nickel, chromium, cadmium, copper, bismuth, lead, and others are either sparingly soluble or dissolve only in an excess of hydrofluoric acid. In the readiness with which fluorine enters into metallofluoric acids is seen another great distinction from the other halogens. In this, as in many of its other properties, it approaches very closely to cyanogen. Hydrofluoric and hydrocyanic acids and their salts have, in fact, little more in common with hydrochloric, hydrobromic, hydriodic acids, and the halogenides, than the fact that they are monobasic or derivatives of monobasic acids.

We have, therefore, in lithium, beryllium, carbon, and fluorine, four typical elements which in the free state, *as elements*, stand in close relationship to the other elements of their respective groups. In two of them, lithium and carbon, the influence of their low atomic weights is not such as to deprive their compounds of the chemical nature which characterizes the derivatives of their analogues. The others, although one of them lies *between* lithium and carbon, and the other has an atomic weight almost large enough to take it out of the typical class, fail to show analogy to their homologues; that is, to satisfy the requirements of the system, as soon as they pass from the free state into combination.

These are contradictions which even the mysterious influence of a low atomic weight will not explain. They were known in 1870, and they stand to-day. With the develop-

ment of organic chemistry, and the increase in the number of bodies known, which could not be explained by the laws of valency alone, stereochemistry appeared. Molecular compounds have been the subject of numerous theories, of which one at least, that of Werner, promises to bear fruit; but the inconsistencies shown, in reference to the other elements, by those of low atomic weight, the exceptions to a law more far-reaching than that of valency itself, have remained untouched, simply in recognition of the fact that it was hopeless to look for any explanation for them, which could be reconciled to the system. And why? Because the inorganic chemist, in standing upon the periodic system, has been unable to dissociate in his mind the chemical compound from the elements of which its formula contains the symbols.

Of the work done in the development of group analogies, little need be said. This has been the only successful field of investigation which the formulation of the system opened. But it may be well to point out briefly certain inconsistencies which are involved in the development of these analogies between neighboring metals in the horizontal rows.

One of the pronounced features of the periodic system is the regularity with which the valency of the elements increases in the successive vertical rows—a regularity to which in fact so much importance is attached, that Mendeléeff can say without fear of criticism, '' PbO_2 is the normal salt-forming oxide of lead, as are Bi_2O_5, CeO_2, TeO_3 of bismuth, cerium, and tellurium !'' According to Mendeléeff, when an element forms two series of compounds, as copper, for instance, in one of which it has the same valency as its neighbor in the horizontal row, its compounds in this degree of oxidation must be similar to those of its neighbor. This rule is well illustrated in the case of copper, for the cupric compounds do bear a very close resemblance to those of the next element, zinc. But examine the rule in its full extension. The formation of an alum by any trivalent metal is rightly regarded as characterizing its behavior throughout all its compounds in this degree of oxidation, and sharply distinguishes its sesquioxide from those of another great class of elements, the rare-earth metals. Associated with the formation of alums is the behavior of the

cyanides toward potassium cyanide. All the sesquioxides[1] which form alums yield soluble double potassium cyanides, the great majority of which have the formula $K_3V(CN)_6$.

In the series,

$$K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni,$$

the most typical double cyanide is formed by iron; that of cobalt is also stable, and on the other side we find an analogous salt formed by manganese, "owing to its proximity to iron." But chromium, beyond manganese, also forms one; and from some experiments which I myself have made, I find also that potassium vanadicyanide, $K_3V(CN)_6$, is not only capable of existence, but a well-defined compound. We have here the character which the atomic weight 56 lends to the compounds of trivalent iron exerting an influence upon that of one element to the right and three elements to the left. With the alums the case is still more remarkable. These bodies are formed by cobalt, iron, manganese, chromium, vanadium, and titanium; or by six of the ten elements in the row. And not only that; scandium, the metal next to titanium, not only forms a sesquioxide, but this is its only degree of oxidation. Its compounds, however, have the properties characteristic, not of ferric and aluminium salts, but of the rare earths. And, nevertheless, the close proximity of this element to titanium does not lend to the trivalent compounds of the latter a single one of the properties of the rare earths. We must seek the influence to which their character is due far over at the edge of the table.

In the foregoing pages no attempt has been made to criticise the analogies which exist, in the various series, between the elements themselves. With this feature of the system little fault can be found. The alkali metals, the alkaline earth metals, Be, Mg, Zn, ··, Ge, Sn, Pb, are thoroughly similar among themselves, and well illustrate the gradation in properties with increasing atomic weight. But with the compounds the case is entirely different. The derivatives of typical elements show no regularity—even in their abnormal

[1] The only exception is in the case of aluminium, the cyanide of which is decomposed by water. Potassium cyanide precipitates the hydroxide.

behavior; the compounds of the 8th group have a decidedly anomalous position. The similarity between the derivatives of elements in states of oxidation uncalled for by the system, either cannot be explained at all, as in the case of lead and barium, magnesium and manganese compounds, or we are forced to ascribe to one or the other series a certain vague, transitive nature. The reason for this lies, not in the principle that the chemical nature of an element and its compounds is a function of its atomic weight, but in our failure to recognize the two-fold character of this principle. We attempt to apply one and the same expression of the law to both elements and compounds. But one has no right, in the systematization of one class of substances, to impose upon himself restrictions which arise only from the system which he employs for another class. No arrangement of the elements according to their atomic weights can be made, which expresses the analogies between the elements themselves, and in which, for instance, magnesium and manganese receive analogous positions. And the result is that, in order to emphasize the relation between zinc and magnesium, which such an arrangement does exhibit, the adherent of the periodic system deliberately closes the door to an explanation of the far closer analogy between the compounds of magnesium and manganese, as if the latter were not conditioned by an equally important law of nature.

A system for the compounds, founded upon the atomic weights of the elements, must also necessarily lead to confusion from another source, for the investigation of the compounds is undertaken solely to characterize the *general chemical nature* of the element. Thus, little distinction is drawn between reactions which do not involve a change in degree of oxidation and those which do. If the two are separated at all, it is only when the resulting compounds are very stable, or else conform to the position of the element in the periodic system. To cuprous compounds, though they are unstable, great importance is attached, because copper belongs to the first family. But, even in so full and scientific a textbook as that of Mendeléeff, the salts of trivalent manganese are reviewed with little more than the passing remark that

they somewhat resemble ferric compounds, and that the chloride decomposes when its solution is warmed. The latter fact seems to deprive the manganic salts of all theoretical interest.

But in a comparison between the derivatives of two metals in the same degree of oxidation, the question of *existence* becomes of more importance than stability, for the latter is often dependent entirely upon external conditions. The fact that bromine is liquid, iodine a solid, at ordinary temperatures, does not prevent the most important analogies being drawn between the physical properties of the halogens in the same state of aggregation, though to obtain bromine and iodine as gases, heat must be employed. So it is with many compounds. They may perhaps be obtained only under, for us, extraordinary conditions, but their very existence may point out in the constituent elements properties which we should otherwise never expect. As an example of such a case only the newly discovered alums of vanadium need be mentioned. The existence of these bodies shows that in spite of the similarity between phosphates and vanadates, the vanadium atom exerts upon the nature of its trivalent compounds the same influence as does iron upon that of the ferric salts. A vanadic solution absorbs oxygen with great avidity, and is therefore called very unstable, but the presence of oxygen is an arbitrarily imposed condition. If oxygen were a rare element, the trivalent salts of vanadium would probably be regarded as its normal compounds, and a vanadate looked upon very much as we look upon ferric acid to-day.

The chemical behavior of an element in a given degree of oxidation must be characterized along two lines. First, by the study of its compounds as mineralogical specimens, their composition, physical properties, solubility, volatility, and the like, together with the reactions which they show without involving change in the degree of oxidation. Secondly, by its passage from this degree of oxidation into others. The first is, in my opinion, by far the more important, for the properties of the compounds of an element in two different degrees of oxidation differ absolutely from one another; and in the two the element appears in entirely different rôles. It

is only after we have ascertained in how far the element can alter its *apparent* character, in corresponding with entirely different elements in different degrees of oxidation, that we can solve its *true* character, and find out a general law for its behavior in all its compounds; and this can be ascertained only by a careful comparison of its compounds with those of other elements in the same degree of oxidation.

A classification based upon this principle, of course, presents great difficulties, owing to the very unsatisfactory extent to which the elements in their unstable degrees of oxidation have been investigated. A thorough study of the compounds, however, has shown that it is capable of giving most interesting results, the nature of which I will discuss in my next article on the subject.

LXV.—THE ACTION OF SULPHUR UPON METAL-LIC SODIUM.

By James Locke and Alfred Austell.

Among the various investigations which have been published regarding the action of sulphur upon metallic sodium, but one is of recent date. Rosenfeld,[1] in a short article relating to the reactions of sodium, confirms the observations of Davy, Gay-Lussac, and Thenard, that the two combine with nearly explosive force, even at the ordinary temperature. Rosenfeld seems to have made no analysis of his reaction-products, but says that by mixing finely divided sodium, sulphur, and sodium chloride together, and rubbing, he obtained a violent reaction, in which a mixture of the monosulphide and polysulphides was formed. His work is accordingly given in the various reference books as indicating a method for preparing sodium monosulphide.

Through a chance observation made while preparing sodium sulphide in some other work, we have been led to study this reaction more closely. As it is practically impossible to separate the products from any sodium which may have been left unaltered in the reaction, a quantitative investigation of their composition is extremely difficult, and

[1] Ber. d. chem. Ges., **24**, 1658.

our results are therefore only approximate. They indicate conclusively, however, that the monosulphide cannot be formed by the direct combination of sodium and sulphur at temperatures below 220°.

Our method of procedure was as follows: A small weighed quantity of clean sodium was covered with about 50 cc. of dry toluene, and the latter heated until the sodium fused. This was carried out in a small flask fitted with a return-condenser and a separatory-funnel. Through the latter the calculated quantity of sulphur, dissolved in hot toluene, was slowly added, while the contents of the flask were kept briskly boiling. The reaction at first results only in a thin yellow film of polysulphide[1] being formed upon the surface of the sodium. It soon grows violent, however; the sodium swells up, and a porous cake of the compound is formed. After this main reaction, which lasts but a few seconds, has subsided, the rest of the sulphur solution was added rapidly, and the mixture boiled for about an hour. The product was then filtered, washed with hot toluene, dried, and tested for sodium. The presence of uncombined sulphur in the mother-liquid could readily be seen from the yellow color of the latter. When no free sodium was found, the substance was submitted to analysis.

Experiments were made successively with two grams of sodium and the quantities of sulphur calculated for the compounds Na_2S, Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5. The results are tabulated below:

Ratios. Na : S.	Sodium. Grams.	Sulphur. Grams.	Product.	Filtrate.
2 : 1	2.0	1.39	Yellow, mixed with much Na	Colorless
2 : 2	"	2.78	"	"
2 : 3	"	4.17	Traces of Na	"
2 : 4	"	5.56	No Na	Yellow
2 : 5	"	6.95	"	"

According to these results the only compound formed at 110°, the boiling-point of toluene, should approximate rather

[1] The fact that this film is yellow shows that even when a great excess of sodium is present no monosulphide forms, as the latter has a red color. In every experiment made, a greenish-yellow product was obtained.

closely to the formula Na_2S_3. That no lower sulphide is formed is clear, and at this temperature metallic sodium has apparently no action upon the polysulphides. In the first two experiments, as the toluene cooled down, the globules of sodium left showed in fact a bright metallic luster. The products of the last two experiments, in which there was no residual sodium, were analyzed by conversion into the sulphate. They had practically the same composition, with 28.89 and 28.57 per cent. sodium respectively. The percentage of sodium calculated for the compound Na_2S_3 is 32.32, and for Na_2S_4, 26.44. Both products were therefore probably mixtures of these two compounds. That more or less of the higher sulphide is formed is also indicated by the fact that the product obtained in the third experiment $(Na : S = 2 : 3)$ contained a small quantity of free sodium.

An experiment was also made in which naphthalene was substituted for toluene, a temperature of 218° being thus obtained. It seemed probable that at this heat a compound containing less sulphur would be formed, if only by the action of sodium upon the polysulphides after the first reaction had taken place. This turned out, however, not to be the case. 2.78 grams sulphur were dissolved in toluene, and added to 2 grams sodium under hot naphthalene. The small quantity of toluene was then distilled off, and the naphthalene kept boiling for an hour. The product contained apparently as much free sodium as that obtained with a mixture of the same proportions at 110°.

New Haven, Conn., May, 1898.

LXVI.—ON SOME COMPOUNDS OF TRIVALENT VANADIUM.

By James Locke and Gaston H. Edwards.

The green solution obtained when vanadic acid is reduced by nascent hydrogen has been but very slightly studied. That it contains salts of vanadium in the trivalent state was recognized by Roscoe[1] in the course of his elaborate investigation on the chemical nature of this element. Roscoe, however, made no attempt to study the products which could be

[1] Ann. Chem. (Liebig), Suppl., **7**, 78.

obtained from the solution which he prepared by dissolving the anhydrous chloride, VCl_3, in water, and failed to make any comparison between that body and the chlorides of other trivalent elements.

The first compounds to be isolated from a vanadic solution were prepared by Petersen,[1] who examined in a very thorough manner the fluoride and its double salts with the fluorides of other metals. His results pointed to a close resemblance between vanadium sesquioxide and its derivatives and the compounds of the groups formed by aluminium, chromium, manganese, and iron. Thus, the compound $K_2VF_5.H_2O$ exhibits in its general properties, solubility, etc., close similarity to the analogously constituted salts of aluminium, iron, chromium, and manganese. Ammonium vanadifluoride, $(NH_4)_3VF_6$, is isomorphous with the ferric salt, $(NH_4)_3FeF_6$, described by Marignac,[2] and Petersen prepared other members of the series in $(NH_4)_3CrF_6$ and $(NH_4)_3AlF_6$. A similar relation was observed between double salts with the fluorides of divalent metals, such as $CoVF_5.7H_2O$, $CoCrF_5.7H_2O$, etc.

Petersen's work and the conclusions drawn from his results were further substantiated by the recent investigations of Piccini[3] on the alums of vanadium. He succeeded in isolating the salts $NaV(SO_4)_2.12H_2O$, $KV(SO_4)_2.12H_2O$, $NH_4V(SO_4)_2.12H_2O$, $RbV(SO_4)_2.12H_2O$, $CsV(SO_4)_2.12H_2O$, and $TlVSO_{42}.12H_2O$. With the exception of a short article by Brierly,[4] who prepared a vanadium sulphuric acid, or 'alum acid,'[5] $V(SO_4)SO_4H.4H_2O$, the above investigations embrace practically all that has been published on vanadic salts.

We have recently undertaken the preparation of a number of other compounds, the analogues of which are of characteristic nature in the case of chromium, in the hope of ascertaining more definitely the influence which the atomic weight of vanadium exerts upon the development of the properties common to the compounds of the group : aluminium, vanadium, chromium, manganese, iron, and cobalt.

[1] J. prakt. Chem. (2), **40**, 44 (1889).   [2] Ann. chim. phys., (3), **60**, 306.
[3] Ztschr. anorg. Chem., **11**, 106; **13**, 441.   [4] J. Chem. Soc. (London), **49**, 822.
[5] Chromium is the only other alum-forming metal which yields such an acid, $Cr(SO_4)SO_4H$.

The chief difficulty which an investigation of this kind presents lies in the extreme readiness with which vanadic solutions absorb oxygen, with formation of vanadyl salts. Petersen was able to start directly from the anhydrous sesquioxide, which is soluble in hydrofluoric acid. The solutions of vanadic sulphate used by Piccini in the preparation of the alums were obtained simply by the electrolysis of vanadic acid
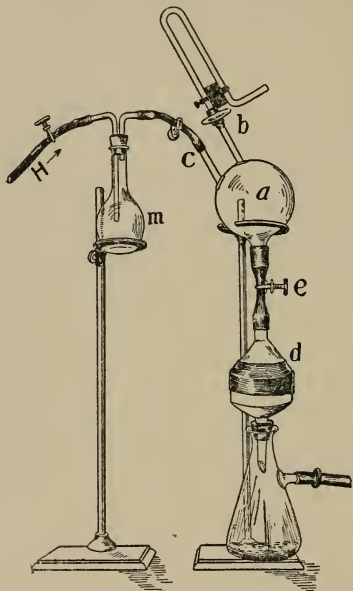
in a solution of sulphuric acid. These methods, while satisfactory in individual cases, are of course limited in their applicability, and they could not be used in the preparation of such compounds as a vanadicyanide, sulphocyanate, or the like. We were therefore compelled to start out from the readily oxidizable vanadic hydroxide, precipitated by an alkali after the reduction of the pentoxide with sodium amalgam.

In order to protect the hydroxide and solutions from oxida-

tion, all operations were carried out in an atmosphere of hydrogen. For this purpose the apparatus shown in the accompanying figure was employed. The pear-shaped bulb *a*, of which we had several pieces, holds about 500 cc. Over its drawn-out end, which is two-thirds of an inch in diameter, passes a piece of thick-walled, soft-rubber tubing, which can be closed by a stop-cock *e*. The tube *b* is of capillary diameter, fitted with a glass cock, and bent over on itself, to more securely prevent the entrance of air when this cock is open. *c* is a somewhat wider tube, which serves for the introduction of reagents, and is closed by a stop-cock when necessary.

For heating on the water-bath, the bulb is placed on the latter, mouth downward, while a rapid current of hydrogen is passed in at *c*, *a* being open. The contents of the bulb may be boiled in a similar manner, the bulb then resting on its side. Reagents are added by means of a small flask *m*, fitted with a cork holding two short tubes, one of which is connected with the hydrogen generator. The reagent having been introduced into the flask (a test-tube is also convenient) the air in the latter is displaced by hydrogen, and the second tube then connected with *c*. The flask is then simply inverted, whereupon the reagent runs into the bulb.

The most important and difficult operation involved in the work was of course the filtration and washing of the vanadic hydroxide. To perform this without exposing the substance to the air, a Buchner's funnel was used, to which was joined by a wide rubber band a well-fitting piece of apparatus, *d*, like an inverted funnel. The stem of the latter was of the same diameter as the mouth of the bulb. Before attaching this filtering-apparatus to the bulb, it was entirely filled, together with the suction-flask, with water, and the latter then displaced by hydrogen. Connection was then made, slight suction applied, and the stop-cock at the mouth of the bulb opened. The precipitate was washed with water from which the air had been expelled by boiling, from a flask connected as for the introduction of reagents.

When the next operation involved the solution of the precipitate in an acid, the filtrate was drawn off by suction

through the pump, the suction-flask rinsed with the water from one or two additional washings, and the acid then introduced as above. The solution was then transferred, either to another bulb, or, if it was to be evaporated to crystallization, to a crystallizing-dish, the side tube of the suction-flask being in that case held below the surface of some benzene placed in the dish.

By taking proper care in the observance of minor details, such as the filling of the tubes with water before making connections, etc., we were able almost entirely to obviate the danger of oxidation; and after a little practice we could carry out the operations of filtration and the like almost as rapidly as in the open air. In one afternoon, starting out with vanadium pentoxide, we have prepared vanadium dihydroxide, $V(OH)_2$, washed it, redissolved in hydrochloric acid, and brought the solution into a desiccator. In spite of all the operations subsequent to the reduction of the vanadic acid, the final solution possessed the true lavender color of vanadious salts, without a trace of green or brown. Roscoe describes such a solution as being a more sensitive reagent towards oxygen than is pyrogallol itself.

The vanadium preparations which we used in this work were placed at our disposal through the kindness of Prof. Paul Jannasch, of Heidelberg, Germany. They consisted chiefly of thoroughly purified vanadates of sodium and ammonium. These compounds were worked up as follows: Enough of the substance to yield about 5 grams of vanadium hydroxide was dissolved in a small quantity of water, 10 cc. of concentrated hydrochloric acid were added, and the solution boiled with alcohol to reduce the vanadic acid to vanadyl dichloride, $VOCl_2$. After the alcohol had been driven off, the solution was transferred to a bulb, and while a rapid current of hydrogen was led through the latter, 5 per cent. sodium amalgam was gradually introduced in small lumps, the solution being in the meantime kept acid by the occasional addition of hydrochloric acid. The reduction was continued until the solution just began to lose the pure green color of the vanadic salts and assume a bluish-green tint, due $_t$o compounds of the next lower degree of oxidation. The

operation required the addition of about 700 grams of amalgam.

The mercury was next drawn off, the solution filtered, transferred to another bulb, and treated in the cold with just enough ammonium hydroxide to precipitate the vanadic hydroxide[1] completely. The latter comes down as a dirty green flocculent precipitate, which absorbs oxygen with the greatest avidity. It was allowed to stand for some time, and then filtered and washed thoroughly with warm water from which the air had been expelled. From this precipitate the following salts were obtained by solution and crystallization.

Vanadium Trichloride, $VCl_3.6H_2O$.—Halberstadt[2] mentions the fact that when the anhydrous chloride, VCl_3, is dissolved in water and the solution evaporated over sulphuric acid, a very unstable crystalline compound is obtained. Piccini mentions in a foot-note to his first article on the vanadium alums[3] that he had obtained this substance in distinct crystals, and found it to have the above composition. This foot-note escaped our notice when first reading his article, and at the time of preparing the compound we supposed we were the first to have isolated it. As, however, nearly three years have elapsed since his article was sent in for publication, we may be allowed to describe the compound, yielding to him the priority of its discovery.

It is obtained by dissolving vanadic hydroxide in concentrated hydrochloric acid and evaporating the green solution to dryness in a vacuum-desiccator. The salt separates out from the sirupy liquid in large green prisms, some of which attained with us the length of nearly half a centimeter. It dissolves in water with extreme readiness, yielding, like the other neutral vanadic salts, a brown solution which becomes green on acidification. The salt is very deliquescent, and on exposure to the air for any length of time, dissolves in the water absorbed and is oxidized to vanadyl dichloride. It is readily soluble in both alcohol and ether, but no distinct crystals could be obtained from its solution in these liquids.

[1] Potassium hydroxide does not work as well for this purpose, as it dissolves more or less of the vanadic hydroxide.
[2] Ber. d. chem. Ges., **15**, 1619 (1882).   [3] Ztschr. anorg. Chem., **11**, 107 (1896).

In the analysis of the substance the solution was acidified with nitric acid and the chlorine precipitated with silver nitrate. The vanadium was determined in another portion by titration from the tetravalent to the pentavalent state with iodine, according to Browning's[1] method. The water was estimated by difference:

	Calculated for $VCl_3.6H_2O$.	Found.
V	19.24	18.96
Cl	40.10	39.95
H_2O	40.66	41.09
	100.00	100.00

An attempt was made to measure the crystals, but they proved too hygroscopic. Their optical properties, however, were found to conform to the rhombic system. Salts of composition similar to that of this compound are seen in $AlCl_3.6H_2O$, $CrCl_3.6H_2O$, and $FeCl_3.6H_2O$.

Potassium Vanadichloride.—An attempt was made to prepare from the chloride a double salt analogous to those of the series $R_2FeCl_5.H_2O$, in which R is K, Rb, NH_4, etc. A few grams of the trichloride were dissolved in concentrated hydrochloric acid, the calculated quantity of potassium chloride added, and the mixture left to crystallize in a vacuum. The product consisted chiefly of green crystals of a somewhat lighter shade than that of the pure vanadium chloride, but it was impossible to isolate these completely. A vanadium determination, made in as pure a product as we could obtain, showed that it contained 22.41 per cent. V. The quantity calculated for the anhydrous compound $KVCl_4$ is 22.03 per cent. V.

Vanadium Bromide, $VBr_3.6H_2O$.—This compound was prepared in a manner strictly analogous to that by which the chloride was obtained, pure concentrated hydrobromic acid being used. It crystallizes with less readiness than the chloride, and decomposes more easily. In other respects the two compounds were closely similar. The bromide decomposes more or less on solution in water, leaving as a residue a small quantity of a brown substance, probably a basic bro-

[1] Ztschr. anorg. Chem., 1, 158.

mide. Like the chloride, it is soluble in both alcohol and ether, to a green solution. The analysis was carried out as in the case of the chloride.

	Calculated for $VBr_3 + 6H_2O$.	Found.
V	12.83	12.62
Br	60.10	59.65
H_2O	27.07	27.73
	100.00	100.00

The iodide could not be obtained. Vanadium hydroxide dissolves in hydriodic acid as readily as in hydrochloric or hydrobromic, but the solution turns brown on evaporation and eventually leaves only an amorphous, brownish-black residue, only partially soluble in water.

Potassium Vanadicyanide, $K_3V(CN)_6$.—For the preparation of this compound, it was found more convenient to start out from the anhydrous vanadium trichloride, which we prepared according to the method of Halberstadt.[1] About 5 grams of this substance were dissolved in as little water as possible[2] and slightly acidified with hydrochloric acid. A concentrated solution of potassium cyanide containing about one and a half times the calculated quantity of the salt was placed in a bulb, and the vanadium chloride solution then added. The mixture at once assumed the form of a thick, deep-purple paste, which gradually became thin again, though without at first losing its color, and remaining almost opaque. This part of the reaction was observed by Petersen,[3] who states that he thus obtained a dark-blue solution. The blue color, however, is in fact due only to very finely divided particles of the original precipitate suspended in the solution, which is itself of a deep wine color. After shaking for some time, the liquid cleared and only a few flakes of a brown residue, presumably the hydroxide, remained undissolved. It is absolutely necessary to have a considerable excess of potas-

[1] Ber. d. chem. Ges., **15**, 1619 (1882).

[2] The formation of the hydrated chloride is readily seen when a quantity of the anhydrous chloride is added to about its own volume of water. It dissolves with a hissing sound, and, on cooling, the liquid solidifies to a green crystalline mass. On addition of more water, this dissolves to a brown solution.

[3] J. prakt. Chem., **40**, 50.

sium cyanide present, as the precipitate dissolves with great difficulty, and a clear solution cannot otherwise be obtained.

The wine-colored solution, after being filtered, was treated with just enough alcohol to bring about incipient precipitation, and then allowed to stand for some hours surrounded by ice-water. A fine precipitate separated out, which consisted of a mixture of potassium cyanide and vanadicyanide, and in addition to this, comparatively large crystals of the latter collected on the sides and bottom of the vessel. These alone were saved, the rest of the product being removed by lixiviation. The crystals were repeatedly washed by decantation with 95 per cent. alcohol, and finally with ether, and dried in a vacuum-desiccator.

In the analysis of the product the carbon and nitrogen were determined by combustion. The vanadium was estimated by titration with iodine, and the potassium as sulphate, in a separate portion, after the oxidation of the vanadium to vanadic acid and its removal as lead vanadate.[1]

	Calculated for $KV(CN)_6$.	Found.
V	15.74	15.89
C	22.22	21.80
N	25.93	26.36
K	36.11	36.47
	100.00	100.52

This salt forms another member of the series of complex cyanides of the formula $K_3M(CN)_6$, of which the other members as yet known are $K_3Cr(CN)_6$, $K_3Mn(CN)_6$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_3Rh(CN)_6$, and $K_3Ir(CN)_6$. The crystals obtained were about a millimeter in length, and of a bright scarlet color. Owing to their instability it was impossible to measure them, and thus determine whether they were isomorphous with the other members of the series. They appeared under the microscope to be rhombic plates, with well-formed domes and base; in polarized light, however, they showed inclined extinction, and are therefore probably monoclinic like the others. In potassium ferricyanide the angle β is 90° 6'.

[1] Roscoe: Ann. Chem. (Liebig), Suppl., 8, 102.

Potassium vanadicyanide is readily soluble in water, insoluble in alcohol. Its aqueous solution grows turbid within a few minutes, however, but is much more stable when containing some free potassium cyanide. Even in that case it cannot be kept for any length of time. The freshly-prepared solution is at once decomposed by acids, turning green. It gives off a slight odor of hydrocyanic acid, as does the solid salt itself. The solution is at first stable toward alkalies in the cold, but on heating or standing for some time the hydroxide separates out.

The solution yields colored precipitates with the neutral solutions of various metals, of which the following are the most distinct :

Ferrous iron,	red-brown.
Cadmium,	yellow.
Copper,	yellow.
Nickel,	purple.
Manganese,	greenish-yellow.

Silver and mercury salts are reduced by it, with deposition of the metals. None of these precipitates is stable toward acids, and their color soon undergoes a change on standing.

We have made repeated attempts to isolate the purple precipitate which separates on the first addition of potassium cyanide to the vanadic solution, but without success. The compound, probably vanadic cyanide, is extremely unstable and on drying yields a green or brown amorphous product, which is obviously a mixture.

The vanadicyanides of ammonium and sodium seem to exist only in solution. Vanadium cyanide dissolves in excess of ammonium cyanide or sodium cyanide, to solutions of the same color as that of the potassium salt. No crystalline products, however, could be obtained from either solution, either by evaporation or precipitation with alcohol. When the latter is employed the compounds decompose at once, with separation of a thick, blue paste.

The properties and reactions of potassium vanadicyanide are of special interest in view of the relative stability of the complex cyanides of the other metals of the group. The only stable compounds of trivalent cobalt are those which contain

the metal as a constituent of a complex radical, either positive, as in the cobaltiamines, or negative, as in $K_3Co(CN)_6$, $H_3Co(CN)_6$, etc. The corresponding ferric compounds, *in comparison with other ferric salts*, are somewhat less stable than the cobaltic compounds as compared with simple cobaltic salts. Thus, for example, potassium ferricyanide is less stable, compared with ferric sulphate, than is potassium cobalticyanide, when compared with cobaltic sulphate. The complex manganese derivatives are relatively still less stable. Among the latter is a sodium salt, $Na_3Mn(CN)_6$, but the free acid is unknown. Chromic cyanide yields neither an acid, $H_3Cr(CN)_6$, nor a sodium salt, and ammonium chromicyanide[1] is very unstable. The chromicyanide solutions, however, are stable towards alkalies even on boiling. In the case of vanadium, neither the sodium nor ammonium salts can be obtained; potassium vanadicyanide is instantly decomposed by acids, with evolution of hydrocyanic acid, and is stable towards alkalies only in the cold. The simple vanadic salts are comparatively stable. Aluminium, which has the lowest atomic weight of all the metals in the group, is precipitated as hydroxide when potassium cyanide is added to its solution, and no cyanogen compounds at all of this metal can be obtained. The tendency to form complex radicals, throughout the entire group, as compared with the tendency to form simple salts, is thus seen steadily to diminish with a decrease in the atomic weights of its members.

Potassium Vanadisulphocyanate, $K_3V(CNS)_6.4H_2O$.—Among the characteristic compounds of trivalent chromium the derivatives of chromic sulphocyanate are very prominent. Potassium chromisulphocyanate, $K_3Cr(CNS)_6.6H_2O$, is almost as stable as the chromicyanide. It is not decomposed by either alkalies or acids in cold solution.[2] A number of other salts, such as $Ag_3Cr(CNS)_6$, $Ba_3[Cr(CNS)_6]_2$, etc., derivatives of the same acid, $H_3Cr(CNS)_6$, are also known.

We have succeeded in preparing a compound of vanadium analogous to this potassium salt, and find that it corresponds very closely to the latter in its reactions. The method employed was as follows :

[1] Ann. Chem. (Liebig), **3**, 163.   [2] Rösler : *Ibid.*, **141**, 185.

An alcoholic solution of potassium sulphocyanate was made by fusing sulphur with potassium cyanide,[1] digesting the product with absolute alcohol, and filtering. To this solution was added somewhat less than the calculated quantity of vanadium chloride, dissolved in a small volume of water. A precipitate of potassium chloride at once appeared, and the solution assumed a deep brown color. After digestion for an hour on the water-bath, the solution was concentrated by evaporation, and then placed in a vacuum-desiccator to crystallize. The first crop of crystals consisted of a mixture of about equal proportions of potassium sulphocyanate and vanadisulphocyanate. This was removed, and the evaporation continued until the solution was of a thick, sirupy consistency. A large quantity of homogeneous, dark-red crystals, almost black, were thus obtained. They were cleaned as thoroughly as possible by pressure between filter-paper, washed with ether, and dried in a vacuum. The analysis gave the following results :

	Calculated for $K_3V(CNS)_6.4H_2O$.	Found.
K	19.90	19.52
C	12.24	....
N	14.29	14.73
S	32.65	33.23
V	8.68	8.55, 8.22, 8.79
H_2O	12.24	13.09
	100.00	

Potassium vanadisulphocyanate, like the corresponding chromium salt, is extremely soluble in both alcohol and water, but is stable only in presence of an excess of potassium sulphocyanate. The pure salt is decomposed by either solvent, forming a green solution. Crystals mixed with a small quantity of sulphocyanate are very hygroscopic, dissolving in the water absorbed. Toward oxygen the salt is the most stable of any which we have prepared. The vanadium in the radical $V(CNS)_6$ undergoes oxidation only very slowly, and in presence of potassium sulphocyanate the solution may be left exposed to the air for some time without losing its character-

[1] Chem. Zeitung, 1866, 666.

istic, dark-brown color. Alkalies precipitate vanadic hy-
droxide from the solution only on boiling, but it is at once
decomposed by acids.

The preparation of corresponding salts of other metals, such
as $Na_2V(CNS)_6$, $Ba_3[V(CNS)_6]_2$, etc., we have not yet
attempted, but we hope to do so in the near future. Our in-
vestigations on the vanadic compounds in general will be
continued.

New Haven, May, 1898.

THE CONDUCTIVITY OF AQUEOUS SOLUTIONS OF PRASEODYMIUM AND OF NEODYMIUM SULPHATES.

By H. C. Jones and H. M. Reese.

The salts used in this work were those which had been
employed by one of us[1] in determining the atomic weights of
praseodymium and of neodymium. The partly purified
compounds were kindly furnished by Mr. Waldron Shap-
leigh. These were further purified by the method described
in the article already cited, and, as there shown, the amount
of impurities which remained in the compounds must have
been small.

The solutions of the sulphates, which had been made from
the oxides, in determining the atomic weights of the metals,
were evaporated to dryness, and heated above the boiling-
point of sulphuric acid, until constant weight was attained.
The salts were then allowed to cool, in weighing-tubes with
ground-glass stoppers, and from these sulphates the following
solutions were prepared.

The water used had been purified from ordinary distilled
water, by the method described by Jones and Mackay,[2] and
was found to have an inappreciable conductivity.

In order to avoid the accumulative error which results
from diluting a solution a large number of times, this was
not repeated very often. A part of the original solution was
diluted three or four times in succession, by removing a
known volume from it, and adding a measured volume of
water. The next dilution was prepared directly from the

[1] This Journal, **20**, 345.   [2] *Ibid.*, **19**, 91.

original solution, in a measuring-flask. This solution was then used as the starting-point in making the following three or four dilutions. The next more dilute solution was made directly from the original solution, and so on.

The Kohlrausch conductivity method, with Ostwald thermostat, was employed, and the cell standardized as usual with $\frac{N}{50}$-potassium chloride, which had been very carefully purified.

A solution of praseodymium sulphate was prepared containing 7.737 grams in 200 cc., which was equivalent to 38.685 grams to the liter. The molecular weight of praseodymium sulphate was taken as 569.1; hence the above solution was 0.06798 normal, or its volume was 14.71. From this solution all the more dilute solutions of this salt were prepared as already described.

The solution of neodymium sulphate which was prepared, contained 11.3595 grams in 500 cc. or 22.7190 grams in a liter. The molecular weight of neodymium sulphate was taken as 575.4, the volume of the above solution being then 25.326. From this, all the more dilute solutions were made.

The dilutions used, and the molecular conductivities found, for both salts, are given in the following table. v is the volume, or the number of liters which contains a gram-molecular weight of the salt, and μ_v, the molecular conductivities.

	Praseodymium sulphate.		Neodymium sulphate.	
	v	μ_v	v	μ_v
1	14.71	98.33	25.33	115.03
2	29.42	117.43	50.65	137.65
3	58.84	141.42	101.31	166.35
4	117.68	169.47	202.61	197.91
5	294.2	217.83	506.5	255.43
6	588.4	262.65	1013.0	303.45
7	1176.8	317.10	2026.0	366.0
8	1471.0	331.43	2532.6	382.9
9	2942.0	403.37	5065.2	462.5
10	5884.0	482.61		

NOTE.

Liquid Hydrogen.

At the meeting of the Royal Society, on May 12, Professor Dewar contributed a preliminary note on the liquefaction of hydrogen and helium.

Professor Dewar said that in 1895 he described apparatus for the production of a jet of hydrogen containing liquid, and showed how such a jet could be used to cool bodies below the temperature that could be reached with liquid air, though all attempts to collect the liquid hydrogen failed. So far, no investigator had improved on the results described in 1895, and as the type of apparatus employed in those experiments worked well, it was resolved to construct a much larger liquid-air plant, and to combine with it circuits and arrangements for the liquefaction of hydrogen. The apparatus took a year to build up, and many months were occupied in testing and in making preliminary trials.

The many failures and defeats need not be detailed. On May 10 an experiment was started with hydrogen cooled to —205° C., and escaping continuously under a pressure of 180 atmospheres from the nozzle of a coil of pipe at the rate of 10 to 15 cubic feet a minute, in a vacuum vessel doubly silvered, and of special construction, surrounded with a space kept below —200° C. With these arrangements liquid hydrogen began to drop from this vacuum vessel into another, doubly isolated by being enclosed within a third, and in five minutes 20 cc. were collected. The hydrogen jet then froze up from the solidification of air in the pipes of the apparatus. The yield of liquid was about 1 per cent. of the gas. In the liquid condition the hydrogen was clear and colorless, showing no absorption-spectrum, and the meniscus was as well defined as in the case of liquid air. The liquid must have a relatively high refractive index and dispersion, and the density must be in excess of the theoretical values; *viz.*, 0.18 to 0.12, deduced respectively from the atomic volume of organic compounds and the limiting density found by Amagat for hydrogen gas under infinite compression. Professor Dewar's old experiments on the density of hydrogen in palladium gave a value for the combined body of 0.62, and it would be interesting to find the real density of the liquid substance at its boiling-point. No arrangements being at hand to determine the boiling-point, two experiments were made to prove the excessively low temperature of the boiling fluid. In the first place, when a long piece of glass tubing, sealed at one end and open

to the air at the other, was cooled by immersing the closed end in the liquid hydrogen, the tube immediately filled, where it was cooled, with solid air.

The second experiment was with a tube containing helium. The Cracow Academy Bulletin for 1896 contained a paper by Professor Olszewski entitled a "Research on the Lique-faction of Helium," in which he stated that, as far as his experiments went, helium remained a permanent gas, and apparently was much more difficult to liquefy than hydrogen. Professor Dewar, however, suggested that hydrogen and helium would probably be found to have about the same volatility, as was the case with oxygen and fluorine. Having a specimen of purified helium, extracted from Bath gas, sealed up in a bulb with a narrow tube attached, he placed the latter in the liquid hydrogen, whereupon a distinct liquid was seen to condense. From this result it would appear that there could not be any great difference in the boiling-points of hydrogen and helium.

In conclusion, Professor Dewar pointed out that all known gases had now been condensed into liquids which could be manipulated at their boiling-points under atmospheric pressure in suitably arranged vacuum vessels, though even so great a man as Clerk-Maxwell had doubts as to the possibility of ever liquefying hydrogen. With liquid hydrogen as the cooling agent, a temperature could be reached within 20° or 30° of the zero of absolute temperature, and its use would open up an entirely new field of scientific inquiry. No one could predict the properties of matter near that zero. Faraday liquefied chlorine in the year 1823. Sixty years afterwards, Wroblewski and Olszewski produced liquid air, and now, after an interval of fifteen years, the remaining gases—hydrogen and helium—were obtained as static liquids. Considering that the step from the liquefaction of air to that of hydrogen is relatively as great in a thermodynamic sense as that from liquid chlorine to liquid air, the fact that the former had been achieved in one-fourth the time needed to accomplish the latter proved the greatly accelerated rate of scientific progress in the present age.

The paper ended with an acknowledgment of the aid rendered by Mr. Robert Lennox, without whose engineering skill, manipulative ability, and loyal perseverance, the present successful issue might have been indefinitely delayed.—*Chemical News.*

REVIEWS.

QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS. BY Dr. ALEX-
ANDER CLASSEN in cooperation with Dr. WALTER LÖB. Authorized
translation, third English, from the revised and greatly enlarged
fourth German edition, by W. H. HERRICK and B. B. BOLTWOOD.
John Wiley & Sons, New York, and Chapman & Hall, London, 1898.

Repeated issue of new editions, both in German and
English, of this useful manual testify to the appreciation
which it has deserved and received. It has clearly taken its
place as one of the standard volumes needed in a working
collection of books on analytical chemistry. The principal
expansion made, in the fourth German edition, of the work
in its earlier form is an extended chapter on the theory of
electrolysis, with detailed explanations in regard to the
bearing of electrode tension, current strength and decomposi-
tion tension on the practical results aimed at. This has
added materially to the value of the book as a systematic
treatise, and the carefully worked over matter on the several
determinations of individual metals will enable anyone to
apply the electrolytic method most satisfactorily to each
particular purpose.

The special examples of crude materials for analysis and their
treatment—omitted from the fourth German edition, but in-
cluded by the translators in the form of an appendix—embrace
some cases for which the (partial) applications of electrolytic
methods must be regarded rather as *tours de force* than as prac-
tically useful processes.

A good feature of the book is the abundant references to
original papers, in which the details of methods, and the
reasons for them, may be fully traced.   J. W. M.

VORLESUNGEN ÜBER THEORETISCHE UND PHYSIKALISCHE CHEMIE.
Von J. H. VAN 'T HOFF. Erstes Heft; DIE CHEMISCHE DYNAMIK.
Mit in den Text eingedruckten Abbildungen. Druck und Verlag
von Friedrich Vieweg und Sohn. 1898. pp. 252.

This book is based upon the course of lectures given by its
author in the University of Berlin, on '' Selected Chapters in
Physical Chemistry.''

The order of treatment which Van't Hoff prefers and adopts
is : First, Chemical Dynamics ; Second, Chemical Statics ;
Third, Relation between Properties and Composition.

The first number, which is now at hand, deals only with
questions in Dynamics, and under the two general divisions
of Chemical Equilibrium and Reaction Velocity. Among the
problems in equilibrium which are discussed, are : Physical
and chemical equilibria between two, three, and four sub-
stances, and chemical equilibrium from the point of view of
molecular mechanics, including homogeneous and heteroge-

neous equilibria. The subject of velocity of reactions is considered under the heads : Reaction-velocity and equilibrium ; the kinetics of reaction, including mono-, di-, and trimolecular reactions ; empirical conditions which affect the velocity of reactions ; effect of temperature on the velocity of reactions ; etc.

The work is appearing at the same time as that portion of Ostwald's *Lehrbuch* (*Verwandschaftslehre*) which deals with many of the same problems, and all who are interested in physical chemistry will regard it as particularly fortunate, that they are furnished simultaneously with two such masterpieces from the hands of the two great leaders in this field.

H. C. J.

REPERTORIUM DER TECHNISCHEN JOURNAL-LITTERATUR. Herausgegeben im Kaiserlichen Patentamt. Jahrgang : 1896. Berlin : Carl Heymanns. Verlag : 1897.

This work is well described in the title. It is characterized by German thoroughness, and while of course it is impossible for the reviewer to verify many of the references, it is fair to assume that it is a reliable guide. It would seem to be indispensable to all who are interested in technical literature. No less than 261 journals are included in the list of those which are referred to in the book. An examination of this list shows clearly, as might have been expected, that nothing of importance is omitted from it. The classification of subjects seems to be a convenient one, and further, there is a full index which will much facilitate the finding of any particular article that may be wanted.

ANIMAL FATS AND OILS, their practical production, purification and uses for a great variety of purposes, their properties, falsification and examination. By LOUIS EDGAR ANDÉS, translated by CHARLES SALTER. Scott, Greenwood & Co., London, 1898.

In this not very large volume, of 231 pages, may be found a good deal of information as to the practical methods of treating animal fats on the industrial scale, the mechanical arrangements for cutting up and " rendering" the crude material, the melting pans, presses, etc., including contrivances intended to diminish the annoyance and improve the sanitary relations of bone-boiling and other offensive branches of the business. The account of recent arrangements for using carbon tetrachloride as a solvent for the extraction of fat is interesting, among the advantages of this solvent being the evident one of its not being inflammable.

A good many expressions are to be found which are open to criticism as more or less inaccurate from a scientific standpoint—*e.g.*, on p. 1 it is said of animal fats, "they are, almost exclusively, compounds of one or frequently several, fatty

acids with glycerine ethers"—on pp. 4 and 179 spermaceti and sperm oil and seal oil are classed under the head of "fish oils"—on p. 11 the formula for oleic acid is given as $C_{19}H_{36}O_2$ —on p. 113 it is stated that by steaming bones a large portion of the "cartilage" is dissolved. Objection may be made to a phrase here and there as not quite defensible English, as on p. 10, "soluble in hot alcohol, ether, benzene, petroleum ether, etc. (at least *in the warm*)", and on p. 21, "oil- and fat-producing seeds and fruits will bear *any length of transport*." The discussion of wool-fat is limited to the organic constituents of "*suint*," no mention being made of the production from it of potash. Statements are repeatedly made in the body of the work as to the results of the examination of individual fats, under such heads as "Reichert number," "Hehner number," "iodine number," etc., without any explanation of the meaning of these terms, such explanation being given only in very condensed form in two or three pages at the very end of the volume.

For the general chemistry of animal (and other) fats, and especially for full details as to their examination by chemical and physical means, several books published within the last few years are much to be preferred—such as F. Jean : Chimie Analytique des Matières Grasses, Paris, 1892 ; R. Benedikt : Analyse der Fette und Wachsarten, Berlin, 1892 ; and C. R. Alder Wright : Animal and Vegetable Fixed Oils, Fats, Butters, and Waxes, London, 1894. This last-named work also gives much information as to industrial processes and plant.

J. W. M.

AMERICAN

Chemical Journal

ON SOME DOUBLE HALIDES OF MERCURY.

By J. N. Swan.[1]

Introduction.

In continuation of the investigations which have been in progress for some years in this laboratory on the so-called double halides, work was begun on the compounds which mercuric chloride forms with the chlorides of the other elements of the second group of the Periodic System. After some months of work upon these, attention was turned to the possibility of forming double salts with the salts of organic bases like aniline and the toluidines ; and the following work was done on these compounds. On account of the more satisfactory results of this work arising from the greater ease of formation and purification of the compounds formed, the description of these will be given first,—the description of the inorganic mercurates being left for the latter part of the paper.

Historical.

Some double halides of metals with the halides of aromatic organic bases have been prepared and described. Destrem[2]

[2] Bull. Soc. Chim., **30**, 482.

prepared an aniline chlorocuprate, $CuCl_2 2(C_6H_5NH_4Cl)$, by adding aniline hydrochloride to an alcoholic solution of cupric chloride. This he describes as a well-behaved salt.

Bibanow[1] prepared an orthotoluidine chlorozincate, $(C_7H_7NH_5Cl)_2ZnCl_2$, by bringing together a concentrated solution of zinc chloride and orthotoluidine hydrochloride, and crystallizing at a temperature of — 5°.

Widmann[2] described a metatoluidine chloroplatinate, $(C_7H_7NH_5Cl)_2PtCl_4$. These salts are also described :

$$(C_7H_7NH_5Cl)_2ZnCl_2(p) ;[3] \quad (C_6H_5NH_5Cl)_2SnCl_4 ;[4]$$
$$(C_7H_7NH_5Cl)_2SnCl_4 ;[4] \text{ and } (C_7H_7NH_5Cl)PtCl_4.[5]$$
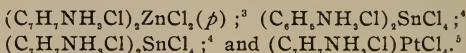
The platinum salt, $C_6H_5NH_5Cl.PtCl_4$, was made by Hofmann[6] by bringing together aniline, hydrochloric acid, and platinic chloride. After describing this salt he attempted to make a mercury salt, but did not proceed in the same manner, and therefore got a salt of a different nature; *viz.*, aniline mercuric chloride ("Kyanolquecksilberchlorid"). In speaking of the properties of this he says : "Auch von Chlorwasserstoffsäure wird es gelöst. Hat man zu wenig Salzsäure zugesetzt, so schmilzt der ungelöste Theil beim Erwärmen zu einem rothen Oele, welches den Boden der Röhre bedeckt. Durch Zusatz von mehr Salzsäure erhält man aber wieder eine klare Lösung aus der sich beim Erkalten schöne weisse Krystalle absetzen. Ich weiss nicht ob diess die unveränderte Quecksilberverbindung ist oder ob Chlorwasserstoffsäure in die Zusammensetzung aufgenommen wurde."

The corresponding iodides, bromides, and cyanides of mercury and other metals are described in a few instances ; *e. g.*,

$$BiI_5C_6H_5NH_3I ;[7] \text{ and } Hg(CN)_2C_6H_5NH_3CN.[8]$$
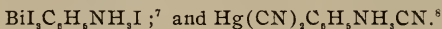
No investigation seems to have been made with the idea of preparing two or more series of salts with the same metal, such, *e. g.*, as $C_6H_5NH_3ClM''Cl_2$, $C_6H_5NH_3Cl2M''Cl_2$, etc. The salts were made by simply bringing solutions together with no particular care as to proportions so that a precipitate

[1] Jsb. Chem., 1874, 747.   [2] Ber. d. chem. Ges., **13**, 677.
[3] Gräfinghoff ; Ztschr. Chem., 1865, 599.   [4] Hjortdahl : Ztschr. Kryst., **6**, 490.
[5] Muspratt, Hofmann : Ann. Chem. (Liebig), **54**, 16.
[6] Ann. Chem. (Liebig), **47**, 62.   [7] Kraut : *Ibid.*, **210**, 323.
[8] Claus u. Merck : Ber. d. chem. Ges., **16**, 2737.

was formed immediately or on cooling. Of course at the time this work was done there was no incentive for making any investigations of this kind. It was simply an open field and no classification was attempted, the only generalization being, '' it has the power to form double salts.''

Wells[1] describes a new class of double salts of the general formula $M'_3M''HI_5$ or $3M'HI$, $M''HI_2$. Although, judging from the analyses given, he did not succeed in preparing very pure specimens of these salts, yet the crystallographic description given by Penfield taken with the description of the salts indicates their reality. The difficulty of the preparation of pure specimens and their recrystallization from a solvent has interfered with the investigation of the possibility of the preparation of salts of this class and other classes, such as $4M'HI.M''HI_2$, etc.

The present class of compounds seemed to be free from this great difficulty to a large degree, and therefore strenuous efforts were made to prepare compounds of the above classes, but in all cases without success, as will be shown later. This is no argument, however, against the existence of such compounds, because these bases vary among themselves as to the classes of compounds formed. This fact gave rise to a great deal of work in the endeavor to get uniform classes of salts with each base. Another question of interest at this time in this line of work is in regard to the possibility of the formation of mixed double halides. Can a salt like $M'M''(Cl)_2Br$ or $M'M''(ClBr)Cl$ exist? Wells[2] has shown the existence of compounds like $Cs(Cl)_2Br$, and used Remsen's hypothesis in their explanation; *viz.*, that two halogen atoms play the part of an oxygen atom. He is led to the conclusion that this couplet can consist of different atoms. In the article above cited[3] Wells describes the preparation of mixed double halides. Here again the difficulty of procuring definite products interfered with the exactness in results which one might desire, but there seems to be good evidence of the existence of these salts.

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[1] Am. J. Sci., **44**, 222.   [2] *Ibid.*, **43**, 31.
[3] *Loc. cit.*

Before this work, Atkinson had described these salts :[1]

$$K_2SbCl_3Br_2l2H_2O; \text{ and } SbCl_3BrKH_2O.$$
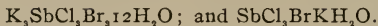
Pitkins[2] described the salt $2KBr.PtCl_4$. Remsen and Richardson,[3] working with potassium-tin salts, were led to the conclusion that the existence of a pure mixed salt of potassium and tin was doubtful. Later, Herty described his fruitless endeavors to prepare mixed double halides with lead and potassium.

During the time that the work on the chlorides about to be described was in progress, work was prosecuted on the attempt to prepare mixed halides. Mercuric bromide was used with the chlorides of the organic bases in each case. Many crops of crystals were obtained—sometimes three sets of them in the same beaker, and for some time it seemed a hopeless task to attempt to get anything definite, but, after many failures, some uniform crops of crystals were obtained at last, and these proved to be mixed double halides.

The following salts are described in this paper :

Aniline Salts.
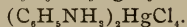
$$C_6H_5NH_3Hg_2Cl_5.$$
$$C_6H_5NH_3HgCl_3.$$
$$(C_6H_5NH_3)_2HgCl_4.$$

Orthotoluidine Salts.

$$C_7H_7NH_3Hg_2Cl_5.$$
$$C_7H_7NH_3HgCl_3.$$
$$(C_7H_7NH_3)_2HgCl_4.$$

Metatoluidine Salts.

$$C_7H_7NH_3Hg_2Cl_5.$$
$$C_7H_7NH_3HgCl_3.$$
$$(C_7H_7NH_3)_2HgCl_4.$$

Paratoluidine Salt.

$$C_7H_7NH_3HgCl_3.$$

Mixed Salt.

$$C_7H_7NH_3HgBr_2Cl.$$
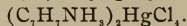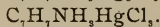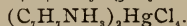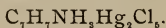
[1] J. Chem. Soc. (London), **43**, (1883), 289.   [2] Chem. News, **47**, 118.
[3] This JOURNAL, **14**, 96.   [4] *Ibid.*, **15**, 81.

Inorganic Salts.
$$MgHg_3Cl_8 + 6H_2O.$$
$$SrHg_3Cl_8 + (H_2O)x.$$
$$BaHg_3Cl_8 + 8H_2O.$$
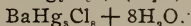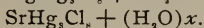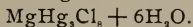
It will be noticed that among the organic salts the class $BHClHgCl_2$ is the only one found with all four bases—the classes $BHCl.2HgCl_2$ and $2BHCl.HgCl_2$ being found with all except paratoluidine (B being used to represent a base, as aniline).

Naming of Compounds.—No complete system of naming the double halides has yet been adopted. The first and second aniline salts are easily named; thus, Dianiline chloromercurate, and aniline chloromercurate. The third might be called aniline dichloromercurate, or aniline chlorodimercurate. In this paper the former will be used and the analogous names in case of the toluidine salts.

Methods of Analysis.—In making analyses of these salts only chlorine and mercury were determined. The estimation of mercury was made by precipitation as sulphide. This required some time for complete precipitation as sulphide, owing to the fact that a yellow, or yellowish white precipitate of sulphochloride is first formed, and care must be taken to have this completely changed to the sulphide. Some free sulphur is sometimes precipitated, but this can usually be dissolved by washing the precipitate with alcohol and then with carbon bisulphide. In making mercury determinations the solutions were acidified with hydrochloric acid. The filters used were washed, dried, and weighed before using, and then the precipitate was weighed on the filter, and the weight of the latter deducted. Satisfactory results were obtained by this method with pure mercuric chloride as a test of the method. Some of the determinations were made in a Gooch crucible. The drying of the precipitate was conducted in an air-bath kept near 90°. Greater difficulty was experienced in getting a satisfactory method for the estimation of chlorine. Owing to the fact that it cannot be estimated in presence of mercuric chloride,[1] it was necessary to remove

[1] See Fresenius' Quant. Analyse, I, 473.

the latter. This was done with hydrogen sulphide. Then the problem of getting out the excess of the latter was to be solved, as it could not be driven off by heat for fear of losing some hydrochloric acid at the same time. After trying several methods it was finally removed as free sulphur by the addition of ammonium ferric alum to the solution, letting it stand for several hours, and filtering. Chlorine was then precipitated as silver chloride, and weighed in a Gooch crucible. In some of the work on the inorganic salts, chlorine was estimated volumetrically, but the gravimetric method gave more satisfactory results. The salts for analysis were purified by treatment with animal charcoal, and recrystallization from water acidified with hydrochloric acid.

ANILINE SALTS.

Aniline Dichloromercurate, $C_6H_5NH_3Hg_2Cl_5$. — Following Destrem's method, aniline hydrochloride was added to an alcoholic solution of mercuric chloride. A salt was formed in irregular crystals while the solution became much colored and some kind of decomposition had evidently taken place which interfered with the purity of the product. The same experiment was performed, using a water solution instead of alcohol. 9 grams of aniline hydrochloride were dissolved in warm water, 20 grams of mercuric chloride were added, and the whole heated and filtered. A salt began to crystallize almost at once. This salt was freed from the mother-liquor and washed with water on the filter-pump. The salt which was formed in alcohol was recrystallized from hot water. Determinations of mercury in both indicated the came compound; *viz.*, Aniline dichloromercurate, $C_6H_5NH_3Hg_2Cl_5$. In the meantime work on the water solutions, which will be described later in connection with the paratoluidine salt, was done, and solutions acidified with hydrochloric acid were used after this. Following these suggestions, aniline hydrochloride and mercuric chloride were mixed in a beaker in molecular quantities for the above salt; then water and a little hydrochloric acid added, and the whole heated to boiling. A beautiful white salt, in sheaves, sometimes in rosettes,

crystallized on cooling. The salt was well washed with cold water on the filter-pump and recrystallized from acidified water solution after treatment with animal charcoal. The salt was analyzed for mercury and chlorine with the following results :

    I. 0.6727 gram salt gave 0.4651 gram HgS.
    II. 0.4727 gram salt gave 0.3263 gram HgS.
    III. 0.7735 gram salt gave 0.8307 gram AgCl.
    IV. 0.8180 gram salt gave 0.8784 gram AgCl.

	Calculated for $C_6H_5NH_3Hg_2Cl_5$.	I.	II.	III.	IV.
			Found.		
Hg	59.62	59.60	59.51	....	....
Cl	26.38	....	....	26.56	26.55

In the first preparation the salt was formed when the aniline hydrochloride was in excess, and the solution boiled. Repeated trials showed that the best results were obtained when mercuric chloride was present in slight excess.

Properties.—Aniline dichloromercurate is much more readily soluble in hot than cold water, being rather insoluble in the latter. It is much more soluble in methyl and ethyl alcohols. It is only slightly soluble in ether. When boiled for some time with alcohol it is decomposed to some extent. Heating to boiling in pure water does not decompose it. The salt is stable in the air if dry, but becomes discolored like many aniline salts if exposed for some time in moist condition.

Aniline Chloromercurate, $C_6H_5NH_3HgCl_3$.—Having obtained this aniline compound in the above manner, the attempt to prepare compounds having a larger, and those having a smaller, proportion of mercuric chloride was next in order. With this end in view, a larger proportion of mercuric chloride was added to constant quantities of aniline hydrochloride. This was carried on until the mercuric chloride would crystallize out with the salt described, and no compound containing a larger proportion of mercuric chloride was obtained. Gradually diminishing the proportion of mercuric chloride, a salt differing from the above was obtained, when molecular quantities of the chlorides were

mixed and the solution not heated too strongly. It was found, however, that there was a tendency to pass into the first form when the solution of equal molecular quantities was boiled. By using a slight excess of aniline hydrochloride the new salt was obtained in better form. The salt was recrystallized from acidified water solution, washed with water on the filter-pump, and dried.

The analyses for mercury and chlorine of the purified salt gave the following results :

I. 0.7509 gram salt gave 0.4365 gram HgS.
II. 0.9662 gram salt gave 0.5585 gram HgS.
III. 0.5662 gram salt gave 0.6114 gram AgCl.
IV. 0.7075 gram salt gave 0.7604 gram AgCl.

	Calculated for $C_6H_5NH_2HgCl_3$.	I.	II.	III.	IV.
			Found.		
Hg	49.98	50.11	49.83	....	....
Cl	26.54	....	....	26.70	26.58

This salt was obtained from ethyl alcohol and from methyl alcohol solutions just as from water solutions. In all cases a small quantity of hydrochloric acid was added. Attempts were made to get better results and larger crystals by using the alcohols and allowing the solutions to evaporate gradually, but with only partial success. The solutions in all cases, except one with methyl alcohol, became very much discolored, and a green substance was continually being formed. This was often filtered off, and the solution cleared by animal charcoal, but only impure crystals were obtained, where they were obtained at all. The crystals seem to have the same general form, whether obtained from water or alcohol solutions.

Dianiline Chloromercurate, $(C_6H_5NH_2)_2HgCl_4$.—By using still smaller proportions of mercuric chloride to constant quantities of aniline hydrochloride, a third salt was obtained with a distinct crystalline form. This salt crystallized in bright glistening needles. It is much more soluble in water and dilute acid than the other salts, and for this reason could not be washed as easily without dissolving considerable of the salt, but it was recrystallized.

Analyses gave the following results :

I. 0.4696 gram salt gave 0.2058 gram HgS.
II. 0.7722 gram salt gave 0.8348 gram AgCl.
III. 0.6849 gram salt gave 0.7373 gram AgCl.

	Calculated for $(C_6H_5NH_3)_2HgCl_4$.	I.	Found. II.	III.
Hg	37.77	37.78	....	....
Cl	26.75	....	26.73	26.62

The salt is obtained most readily and without danger of the salt with more mercuric chloride being formed, if aniline hydrochloride is added in excess to the original solution.

Properties.—Dianiline chloromercurate is much more soluble than either of the above described chloromercurates. Concentrated solutions must be used in its preparation. By addition of the proper amount of mercuric chloride and boiling, it can be converted into aniline chloromercurate.

The process of adding a larger proportion of aniline hydrochloride was continued still further in different proportions, but no other compound was obtained. This last-described salt was always formed and then aniline hydrochloride would crystallize out mixed with the crystals of the salt. Repeated attempts with varying conditions of temperature, dilution, acidification, and proportions of ingredients gave the same results. We conclude that a salt with a larger proportion of aniline hydrochloride than is found in dianiline chloromercurate cannot be made by this method. No other method was tried. It was noted sometimes in the heating of the solutions from which the above salts crystallized, and always when they were slowly evaporated by heat, that a flocculent green substance was formed in the solution. This floated about and had to be separated by filtration. Owing to lack of time this has not been investigated, and the exact conditions suited to its formation were not learned. It was usually much more abundant in the alcoholic solutions. It was observed that the salts with smaller proportions of mercuric chloride can be converted into those with larger proportions. On the other hand, the latter can be converted into the former by the addition of aniline hydrochloride. This is not as easily

accomplished, however, and the aniline chloride must be added in excess and the solution boiled longer. Aniline dichloromercurate seems to be the salt most easily formed.

The mother-liquors from which these salts crystallized were slowly evaporated to learn if salts of different composition could be formed, but nothing new was found in this way. Sometimes a second crop of crystals of the salt first formed was obtained, but usually mixtures of the salts, or of the salts and the simple chlorides were formed.

ORTHOTOLUIDINE SALTS.

Orthotoluidine Dichloromercurate, $C_7H_7NH_2Hg_2Cl_5$.—Following the indications of the experience with the aniline salts, nearly molecular quantities, for the above formula, of orthotoluidine hydrochloride and mercuric chloride were brought together in acidulated water solution, with the mercuric chloride in slight excess. A salt crystallized out on cooling. The first part of the crystallization was in irregular, ragged plates, and on top of these a few needles of prism-like crystals were deposited during the night. The two sets of crystals having apparently different solubilities, water was added, the solution heated and allowed to crystallize again, but with the same result. A new solution was made and it acted in the same way. One of these solutions was heated and the ragged crystals were again deposited on cooling. The mother-liquor was poured off and the crystals were washed with the aid of the filter-pump. The mother-liquor after a time began to form the prism-like crystals. These were also separated and washed. Estimations of mercury in the two salts indicated that both had the same composition; *viz.*, $C_7H_7NH_2Hg_2Cl_5$. Thinking the different forms of crystals were due to some impurity— possibly some para salt present,—a new start was made. The orthotoluidine first used was marked C. P. Some more of this was taken and treated with oxalic acid, and then by crystallization separated from any possible para salt present. The oxalate was then treated with a base and redistilled with steam. By this means a pure base was obtained and by treatment with pure hydrochloric acid and recrystallization, a

most beautiful salt was obtained. On making the double salt, using this chloride, the crystals were deposited in beautiful leaf-like forms in which the veins extended beyond the border, giving a ragged edge. This was the general form first observed. There semed to be no tendency to form the other crystals in this case. The salt was then recrystallized and analyzed with the following results :

I. 0.5973 gram salt gave 0.4054 gram HgS.
II. 0.6948 gram salt gave 0.4703 gram HgS.
III. 0.6740 gram salt gave 0.7096 gram AgCl.
IV. 0.9160 gram salt gave 0.9663 gram AgCl.

	Calculated for $C_7H_7NH_3Hg_2Cl_5$.	I.	II.	Found. III.	IV.
Hg	58.40	58.51	58.35	....	....
Cl	25.85	....	....	26.04	26.09

Orthotoluidine Chloromercurate, $C_7H_7NH_3HgCl_3$.—Several attempts to make the above were, at first, unsuccessful. In fact, it was at first obtained by evaporating the mother-liquor from a crystallization of orthotoluidine dichloromercurate in which the organic chloride was in excess. By using a slight excess of the toluidine chloride, and only heating to the boiling-point, the salt was obtained.

Analyses of the purified salt gave these results :

I. 0.5802 gram salt gave 0.3247 gram HgS.
II. 0.5724 gram salt gave 0.3194 gram HgS.
III. 0.7748 gram salt gave 0.8111 gram AgCl.
IV. 0.6999 gram salt gave 0.7313 gram AgCl.

	Calculated for $C_7H_7NH_3HgCl_3$.	I.	II.	Found. III.	IV.
Hg	48.30	48.24	48.10	....	....
Cl	25.65	....	....	25.89	25.84

Properties.—As regards its solubility and general properties this salt is very much like the corresponding aniline salt.

Diorthotoluidine Chloromercurate, $(C_7H_7NH_3)_2HgCl_4$.—This salt was readily formed by bringing the ingredients together in about the calculated proportions for the formation of the salt, but with the organic chloride in slight excess. A *small* amount of acidulated water must be used as the salt is quite

soluble in cold water. It is not so readily purified as the others on account of the fact that it is so soluble as to preclude much washing. The salt crystallizes in bright, glistening needles or prisms, which are usually collected in rosettes. It is quite soluble in alcohol, and soon colors the solution on heating, showing decomposition. This is characteristic of the chlorides of the formula $(BH)_2HgCl_4$. They seem less stable than the halides with a larger proportion of mercuric chloride.

Analyses of the purified salt gave :

I. 0.5552 gram salt gave 0.2333 gram HgS.
II. 0.6308 gram salt gave 0.2637 gram HgS.
III. 0.4591 gram salt gave 0.4780 gram AgCl.
IV. 0.5974 gram salt gave 0.6169 gram AgCl.

	Calculated for $(C_7H_7NH_3)_2HgCl_4$.	I.	II.	III.	IV.
			Found.		
Hg	35.88	36.22	36.04	....	....
Cl	25.41	....	....	25.75	25.54

The properties of the orthotoluidine salts are much like those of the corresponding aniline salts. The intermediate salts are more difficult of preparation than the others, because of the ease with which they pass into the salt with more mercury on the one hand, and the liability of the formation of some of the salt with a less amount of mercury on the other. As in the case of the aniline salts, the toluidine salts become discolored on standing only a short time in solution. In the formation of dianiline chloromercurate and diorthotoluidine mercurate, particularly, is this the case. With these the flocculent green substance before mentioned was most abundant. As before, attempts were made to get a salt with a larger proportion of the organic chloride, but without success, although many efforts were made. There were no indications of a fourth salt in any case. Some beautiful six-sided plates were often formed, but these always proved to be pure orthotoluidine hydrochloride.

METATOLUIDINE SALTS.

Metatoluidine Dichloromercurate, $C_7H_7NH_3Hg_2Cl_5$. — The above salt was readily obtained in the same manner as the

corresponding salts already described. It was purified in the usual manner and analyzed with these results :

I. 0.4198 gram salt gave 0.2856 gram HgS.
II. 0.5938 gram salt gave 0.4027 gram HgS.
III. 0.4954 gram salt gave 0.5207 gram AgCl.
IV. 0.4874 gram salt gave 0.5119 gram AgCl.

	Calculated for $C_7H_7NH_2Hg_2Cl_6$.	I.	II.	III.	IV.
			Found.		
Hg	58.40	58.65	58.46	....	....
Cl	25.85	....	....	25.99	25.97

Properties.—Metatoluidine dichloromercurate crystallizes in thin plates or scales. It is very much like the corresponding aniline and orthotoluidine salts in solubility and other properties. The meta salt seems less soluble than the others. The crystallization took place soon after the solution began to cool—a certain temperature, rather than a certain concentration of solution, seeming to determine the point of saturation. The salt would all crystallize near this temperature. This was true of solutions of quite different concentration.

Metatoluidine Chloromercurate, $C_7H_7NH_2HgCl_3$. — The amount of metatoluidine at hand did not permit of as thorough an investigation of this salt as was given to those before described. This intermediate salt is the only one which suffered, however, from lack of material. It is the most difficult to get, and therefore required more of the ingredients used. One or two crops of crystals were obtained in small quantity, which had a satisfactory appearance. They were not recrystallized, however, and the analyses below are of the specimens of these crystallizations. The crystals which had a light-purplish color (probably due to impurities) formed in very thin plates which reached across the beaker, and broke up into scales when taken out.

Analyses of the specimen gave the following results :

I. 0.4126 gram salt gave 0.2289 gram HgS.
II. 0.4906 gram salt gave 0.2737 gram HgS.
III. 0.5730 gram salt gave 0.6031 gram AgCl.
IV. 0.6486 gram salt gave 0.6774 gram AgCl.

	Calculated for $C_7H_7NH_3HgCl_3$.	I.	Found. II.	III.	IV.
Hg	48.30	47.82	48.13	....	....
Cl	25.65	....	....	26.03	25.83

Dimetatoluidine Chloromercurate, $(C_7H_7NH_3)_2HgCl_4$.—This salt was made in the usual way. It crystallized in thin glistening scales with grayish luster. Little need be said of it as it closely resembles the corresponding salts already described.

Analyses of the purified salt gave these results:

I. 0.4316 gram salt gave 0.1801 gram HgS.
II. 0.5152 gram salt gave 0.2147 gram HgS.
III. 0.4844 gram salt gave 0.5004 gram AgCl.
IV. 0.4851 gram salt gave 0.5002 gram AgCl.

	Calculated for $(C_7H_7NH_3)_2HgCl_4$.	I.	Found. II.	III.	IV.
Hg	35.88	35.97	35.92	....	....
Cl	25.41	....	....	25.55	25.55

Paratoluidine Chloromercurate, $C_7H_7NH_3HgCl_3$. — About equimolecular quantities of the two chlorides were weighed into a beaker and water added. On heating gradually, a salt suddenly separated out which completely filled the space occupied by the liquid. This was dissolved on further heating, and the salt crystallized out on cooling. As there was some doubt as to the homogeneousness of the deposit, much more water was added, and a second crystallization was made. This appeared to give two sets of crystals, one more soluble than the other.

By adding more water and watching the process of separation of the crystals, the less soluble salt was obtained. A determination of mercury indicated the salt $C_7H_7NH_3HgCl_3$. Other trials seemed to indicate that a pure uniform salt could not be obtained with water alone. It either decomposed the salt formed or caused the action to proceed in such a manner as to form more than one salt. It was here found that, if the solutions were acidified with hydrochloric acid, uniform crystallizations could be obtained. Following the suggestion of these experiences, the salt was made by bringing together molecular quantities of paratoluidine hydrochloride and mer-

curic chloride. Water and a little hydrochloric acid were added and the whole gently heated. In a few minutes a precipitate was formed which filled the whole solution. On heating higher this dissolved, and readily crystallized on cooling in beautiful white needles. The needles were usually collected into sheaves or rosettes, but were sometimes alone. The salt was usually colored, unless the solution was treated with charcoal before crystallizing.

Analyses of the purified compound were made with the following results :

I. 0.7092 gram salt gave 0.3987 gram HgS.
II. 0.2581 gram salt gave 0.1454 gram HgS.
III. 0.6195 gram salt gave 0.6456 gram AgCl.
IV. 0.6567 gram salt gave 0.6867 gram AgCl.

	Calculated for $C_7H_7NH_2HgCl_3$.	I.	II.	III.	IV.
		Found.			
Hg	48.30	48.46	48.56	....	....
Cl	25.65	....	....	25.77	25.86

Properties.—Paratoluidine chloromercurate is much more soluble in hot than cold water, and can, therefore, be readily crystallized. It is more easily soluble in methyl and ethyl alcohols, but is insoluble in ether. The salt can be washed very thoroughly with cold water on the filter-pump, and this method was used. It was dried by pressing between layers of drying-paper. By crystallizing slowly, beautiful needles, nearly three inches long, were obtained. On exposure for a little time in the air of the laboratory in a moist condition, they assume a rose tint, and become more discolored on longer standing. When thoroughly dried they assume a very slight brownish or cream tint on standing in a weighing-tube.

Next, a solution of the original chlorides in the proportion of one molecule of paratoluidine hydrochloride to two of mercuric chloride was made, when the same salt was obtained. This solution was boiled for some time, and solutions with this proportion of chlorides, and with varying amounts of hydrochloric acid were made, but the same results were always obtained. A salt of the composition $C_7H_7NH_2Hg_2Cl_5$

in the cases of the ortho and meta compounds and a corresponding aniline salt having been obtained, strenuous efforts were made to get a similar para compound by these methods. The excess of mercuric chloride was gradually increased in successive trials until it began to crystallize out with the salt originally obtained, mixed with it. It seemed strange that in each of the other cases a compound containing one molecule of the basic chloride to two of the mercuric chloride could be obtained, while with the para compound it could not be formed. It could not be obtained by these methods, however, although the conditions were varied through wide ranges as to the excess of mercuric chloride, the amount of water used, the amount of acid added, and the degree of heat employed. This fact suggested the idea that there might be a greater possibility in the other direction with the para compound than with the ortho and meta. With this in view experiments were next made using an excess of the basic chloride in gradually increasing amounts and under varying conditions. The results were invariably the same. The salt above described was formed in every case in quantity sufficient to use up the mercuric chloride, and on evaporation the excess of paratoluidine hydrochloride crystallized from the solution. The salt $C_7H_7NH_2HgCl_3$ is therefore the only paratoluidine chloromercurate which it seems possible to make by these methods. The para salt, on account of its insolubility in cold water and the ease with which it can be crystallized, was probably the most satisfactory of the salts obtained. In its formation it was free from any admixture of the salts having different proportions of the chlorides—a fact which gave trouble, sometimes, in working with the other salts.

MIXED DOUBLE HALIDES.

No complete investigation has been made in this line, but a few words will be given in order to show the nature and tendency of the work.

4 grams of orthotoluidine hydrochloride and 12 grams of mercuric bromide were weighed into a beaker with about 75 cc. of water, and a few drops of hydrochloric acid added.

(Numerous attempts with water only were failures.) Some mercuric bromide crystallized out and was removed. On longer standing a salt crystallized in beautiful, glistening needles. These were uniform and regular in appearance, and were washed and dried.

Estimations of mercury gave:

	Calculated for $C_7H_7NH_3HgBr_2Cl$.	I.	Found. II.
Hg	39.76	40.11	40.51

The existence of mixed halides of this order seems undoubted. The only difficulty is to get them in good condition. The above is given to show the possibility of their formation.

When a chloride and bromide of the above kinds are mixed there are a number of possibilities—any of these salts may be formed: $HgBr_2$, $HgCl_2$, $C_7H_7NH_3HgBrCl$, $C_7H_7NH_3HgBr_2Cl$, and several others which might crystallize out. In some of the experiments all these possibilities seem to be realized in the same beaker, judging from the various crystals formed.

Some of the salts when heated in the mother-liquor melt to heavy oils which sink to the bottom of the beaker. These oils crystallize on cooling, but they have not been fully investigated. At present the most that can be said is that there is no doubt in the mind of the author as to the existence of the mixed salts, and the work on them will be continued.

CHLOROMERCURATES OF ELEMENTS OF THE SECOND GROUP.

The following salts have been described by Von Bonsdorff:[1]

$$HgCl_2.MgCl_2 + 6H_2O.$$
$$3HgCl_2.MgCl_2 + 5H_2O.$$
$$HgCl_2.ZnCl_2 + 4H_2O.$$
$$2HgCl_2.CaCl_2 + 6H_2O.$$
$$5HgCl_2.CaCl_2 + 8H_2O.$$
$$2HgCl_2.SrCl_2 + 2H_2O.$$
$$2HgCl_2.BaCl_2 + 2H_2O.$$
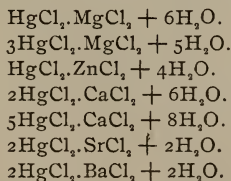
Analyses are given for all except the zinc and strontium salts. The general method of preparation used by Von

[1] Ann. Phys. (Pogg.), **17**, 115.

Bonsdorff was to add mercuric chloride, as long as it would dissolve in the cold, to a saturated solution of the other chloride in water. Then by slow evaporation he would obtain two salts from the same solution, the second crystallizing after the first had been removed. His analyses were performed in a tube or bulb prepared for the purpose. The method in general was this : A weighed quantity of the salt to be analyzed was placed in this weighed bulb, and heated to drive off the water of crystallization which was collected in a calcium-chloride tube and weighed, or allowed to escape, and estimated by the difference in weight of the bulb. Higher heat was now employed, and the mercuric chloride driven off, and estimated either by difference or by having it sublime in another part of the apparatus. The residue gave the basic chloride. Considering the method, his results agree very well indeed with the calculated. The chief difficulty in the prosecution of this work was, as has been the case with much of the work on the double halides, to get pure salts. The salts are so very soluble that when they do crystallize it is difficult to know whether you have a uniform salt or not. In this investigation more work was done upon the magnesium salt than upon any other. The methods of preparation were, in general, used by Von Bonsdorff with some variations. The methods of analysis for mercury and chlorine were those given in the earlier part of this paper. Magnesium was precipitated as pyrophosphate, strontium as carbonate, and barium as sulphate.

Magnesium Salt.—Following Von Bonsdorff's directions, mercuric chloride was added to a saturated solution of magnesium chloride. This was heated and filtered. On allowing to stand, or on evaporating slowly, a set of crystals were deposited just as Von Bonsdorff describes them. It is almost impossible to free this salt completely from the mother-liquor. The method pursued was to place it first on the filter-pump, and then quickly remove it and press it between thick folds of drying-paper by means of a press.

The formation of the salt was tried a great many times and a great many products were analyzed. In order to learn

whether the water of crystallization could be driven off by heat or not, about a gram of the salt was carefully weighed and put into an air-bath. Heated for eighteen hours at not over 105°, it lost 20.79 per cent. in weight. Continuing the drying for fifteen hours more with the temperature at no time above 102°, the salt lost 46 per cent.

Another specimen lost 20 per cent. while at a temperature of not over 100°. A third specimen lost 12.6 per cent. when dried at a temperature of not over 90°.

Mercuric chloride itself lost about 20 per cent. dried at 90° or below in fifteen hours, and over 65 per cent. when at the same temperature for two or three days.

From these experiments it will be seen that it is impossible to determine the water of crystallization by heating. As the salt does not lose its water of crystallization over sulphuric acid, it could not be determined in this way. The average of a number of analyses of the better specimens obtained gave the following results :

	Calculated for $MgHg_3Cl_8 + 5H_2O$.	Calculated for $MgHg_3Cl_8 + 6H_2O$.	Found.
Hg	60.18	59.11	59.22
Mg	2.40	2.36	2.58
Cl	28.41	27.90	27.02

Von Bonsdorff's analyses calculated with the same atomic weights give :

I.	Hg	60.08	Mg	2.46	Cl	28.52
II.	Hg	59.68	Mg	2.43	Cl	28.28

From these figures he deduces the formula with five molecules of water. The formula with six molecules, as is seen, agrees better with the results obtained at this time, but the results are not sufficiently accurate to say with certainty that it has six molecules of water. Von Bonsdorff describes a salt obtained by evaporation of the mother-liquor from this salt. No such salt was obtained, although many and varied attempts were made to obtain it. Solutions were evaporated slowly for days, others more slowly for weeks, and others still more slowly for months, and no such salt was formed. After the first salt ceased to separate in good form all other crystal-

lizations were mixtures of such a nature as to preclude separation. They were, as nearly as could be learned, mixtures of the first salt and one of the chlorides added in the first place. Attempts were also made to form other salts by using varying proportions of the other two chlorides, and by varying the amount of acidification and of dilution, etc.—all with no success.

Some investigations were begun on the chlorides of the other elements of the group. On account of the unfinished condition of the work, only the compounds of strontium and barium will be mentioned.

Strontium Salt.—The chlorides of strontium and mercury were brought together as in making the magnesium salt. A crystallized salt was obtained which is very soluble. It crystallizes in transparent plates, but sometimes in very delicate needles or hairs which project from the top of the solution. This latter was the case when a solution at the point of saturation stood in the air. In the morning there would be a crop of these hairs which would dissolve by the heating of the room during the day and re-form again in the night.

Four analyses of good specimens of this salt gave :

| Hg | I. | 50.48 | II. | 50.59 | III. | 50.49 | IV. | 50.35 |
| Sr | I. | 8.90 | II. | 8.94 | III. | 9.22 | IV. | 9.13 |

The salt loses water over calcium chloride or sulphuric acid. Several weighed specimens left for some days over sulphuric acid lost from 13.30 per cent. in the case of the smallest amount, to 14.16 per cent. in the case of the largest. Von Bonsdorff gives $SrCl_2.2HgCl_2 + 2H_2O$ as the composition of this salt, but the conclusion arrived at in this work was that it is a compound of the same order as the magnesium salt ; *viz.*, $SrHg_3Cl_8 + (H_2O)x$.

No other salt was obtained, although a number of attempts were made to form one.

Barium Salt.—A barium salt was formed in the same manner. This, like the strontium salt, lost water even on standing in the air, so that it had to be analyzed immediately after its formation. Two specimens were analyzed after recrystallization with these results :

	Calculated for $BaHg_3Cl_8 + 8H_2O$.	Found.	
		I.	II.
Hg	51.54	51.87	51.63
Ba	11.77	11.84	11.89

This barium trichloromercurate is less soluble than the other salts, and can, therefore, be prepared more easily and surely.

All the double halides described in this article obey Remsen's law,[1] and all attempts to prepare salts not obeying the law, failed.

THE DOUBLE HALIDES OF TIN WITH ANILINE AND THE TOLUIDINES.

By ROBERT L. SLAGLE.[2]

Introduction.

The object of this work was to prepare and study the double chlorides formed by the chlorides of tin with the chlorides of aniline and the toluidines. There are two records in the literature of work done on these compounds, Hofmann[3] says, "Erwähnen will ich noch eines sehr schönen Doppel-salzes, welches chlorwasserstoffsaures Chloranilin mit Zinn-chlorür bildet. Beim Vermischen beider Auflösungen bleibt die Flüssigkeit klar, nach einiger Zeit aber erstarrt sie zu einer silberglänzenden Krystalmasse." Hjortdahl[4], prepared and made a crystallographic study of the salts, $(C_6H_5NH_2)_2H_2SnCl_6$ and $(p\text{-}C_7H_7NH_2)_2H_2SnCl_6$, but says nothing of the method of preparing them or of their chemical properties.

The number of recorded double halides of inorganic with organic halides is comparatively small. All of them fall under Remsen's law except the salt $CuCl_2.5C_7H_8N.HCl$, which was described by E. Pomey.[5] No efforts have as yet

been made to prepare this salt in this laboratory, but it will receive attention in the course of time.

In the table below the formulas of the salts described in this paper are given:

Aniline Salts.
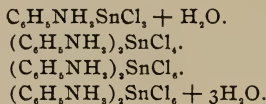
$C_6H_5NH_3SnCl_3 + H_2O.$

$(C_6H_5NH_3)_2SnCl_4.$

$(C_6H_5NH_3)_2SnCl_6.$

$(C_6H_5NH_3)_2SnCl_6 + 3H_2O.$

Metatoluidine Salts.

$C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O.$

$(C_7H_7NH_3)_2SnCl_6 + H_2O.$

Orthotoluidine Salts.

$C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O.$

$(C_7H_7NH_3)_2SnCl_6 + 2H_2O.$

Paratoluidine Salts.

$C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O.$

$(C_7H_7NH_3)_2SnCl_4.$

$(C_7H_7NH_3)_2SnCl_6 + H_2O.$
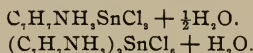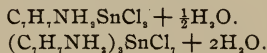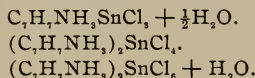
Methods of Analysis.—The salts were purified for analysis by recrystallization from water acidulated with hydrochloric acid. Determinations of tin and chlorine only were made. After the salt was weighed it was dissolved in water acidulated with a few drops of sulphuric acid. Hydrogen sulphide was passed through slowly for about three hours, and in each case the precipitate stood in the solution over night. The stannous or stannic sulphide was collected on a washed filter, dried and ignited in a weighed porcelain crucible. A small amount of concentrated nitric acid was then added and evaporated slowly. The oxidation was completed by igniting over the blast-lamp. A few small pieces of ammonium carbonate were added to remove any traces of sulphuric acid that might be present. After another ignition the crucible was allowed to cool in a desiccator. The tin was weighed as stannic oxide.

As chlorine cannot be determined in the presence of tin,

the tin was removed as sulphide. The problem now was to remove the excess of hydrogen sulphide that remained in the solution. At first this was done by adding cadmium sulphate and precipitating the hydrogen sulphide as cadmium sulphide. This gave satisfactory results, but the following more convenient method was adopted. A stream of carbon dioxide was passed through the solution about two or three hours. This was afterwards heated and allowed to boil for a short time. Silver nitrate was now added. After standing for a time the precipitate was collected in a weighed Gooch crucible, dried in the air-bath at 160°, and weighed.

Preliminary Experiments.—In order to decide upon the best solvent for the preparation of the double chlorides, preliminary experiments were tried with water, methyl alcohol and ethyl alcohol, each being acidulated with hydrochloric acid. The chlorides of tin and the aniline and toluidine hydrochlorides were each dissolved separately, heated, and mixed when near the boiling-point. The mixture was then allowed to boil for a minute or two and placed aside to cool. In each case a salt was formed. Although the salts crystallized from the alcohols, they were so extremely soluble, that in the preparation of all the compounds described in this paper, water alone, acidulated with hydrochloric acid, was used as the solvent. As to the manner of working, many points were obtained from the experience of Swan.[1]

ANILINE SALTS.

Aniline Chlorostannite, $C_6H_5NH_3SnCl_3 + H_2O.$—For the preparation of this compound molecular quantities of aniline hydrochloride and stannous chloride were separately dissolved in water acidulated with hydrochloric acid. Each solution was heated very nearly to the boiling-point ; then they were mixed and allowed to boil for a short time. The beaker was set aside to cool. The solution remained clear until the next day, when it was slightly disturbed, and in a moment changed into a mass of beautiful silver-white crystals. As it was impossible to distinguish individual crystals, this mass was redissolved, diluted, and again set aside. The day following,

[1] See preceding article.

the beaker contained a number of transparent, colorless crystals, spear-like in form, and grouped about several centers. They were removed from the mother-liquor, dried, and re-crystallized.

Similar experiments were tried, in the one case with aniline hydrochloride, slightly in excess of molecular proportions, and, in the other case, with slight excess of stannous chloride. Crystals were obtained similar to those first described, with this exception that those crystallizing from the solution in which the aniline hydrochloride was in excess are somewhat more opaque than the others. The analyses revealed no difference in composition.

After the salts were recrystallized they were filtered with the aid of the pump, and afterwards set aside between folds of drying-paper. They were then analyzed for tin and chlorine with the following results :

I. 0.3824 gram salt gave 0.1718 gram SnO_2.
II. 0.3161 gram salt gave 0.1410 gram SnO_2.
III. 0.3161 gram salt gave 0.4011 gram AgCl.
IV. 0.2567 gram salt gave 0.3263 gram AgCl.

	Calculated for $C_6H_5NH_3SnCl_3 + H_2O$.	I.	II.	III.	IV.
			Found.		
Sn	35.28	35.15	35.16	....	....
Cl	31.51	....	....	31.38	31.43

Properties.—Aniline chlorostannite dissolves slowly in cold water, but very readily in hot water. In a short time these solutions become turbid, probably in consequence of the formation of a basic chloride of tin. It is easily soluble in dilute hydrochloric acid, nitric acid, and sulphuric acid, also in concentrated hydrochloric acid, and nitric acid, but very slightly soluble in cold, concentrated sulphuric acid. The nitric-acid solutions turn yellow when heated, and give off the odor of phenol or a nitro-phenol. The salt is extremely soluble in methyl and ethyl alcohols, coloring the latter yellow, but almost insoluble in ether.

When heated, the salt begins to decompose at about 70°, as is shown by the condensation of white fumes upon the sides of the tube in which it is heated. At about 110° the salt

melts and changes to a yellow color. Some of the salt was heated to a higher temperature; a white crystalline product was deposited on the sides of the tube. This was collected and analyzed for chlorine.

0.0678 gram gave 0.0756 gram AgCl, which corresponds to 27.59 per cent. Cl. Calculated Cl for $C_6H_5NH_3Cl$ is 27.39 per cent. From this we conclude that when heated the salt breaks down into stannous chloride and aniline hydrochloride.

One of the beakers containing crystals of the aniline chlorostannite in the hydrochloric-acid mother-liquor was allowed to stand for a time in a desiccator. The crystals gradually went into solution. After four weeks new crystals which had formed in tufts were taken out, dried, and analyzed. When hydrogen sulphide was passed through the solution, yellow stannic sulphide was precipitated. The crystals were not pure, and hence did not give sharp results.

I. 0.2227 gram salt gave 0.0623 gram SnO_2.

II. 0.1228 gram salt gave 0.2033 gram AgCl.

	Calculated for $(C_6H_5NH_3)_2SnCl_6$.	Found. I.	II.
Sn	22.89	22.00	....
Cl	40.91	....	40.94

These results show that in hydrochloric-acid solution $C_6H_5NH_3SnCl_3 + H_2O$ passes over into $(C_6H_5NH_3)_2SnCl_6$, from the stannous to the stannic condition.

Crystallography of the Salt.[1]—The crystals of aniline chlorostannite are tabular in habit, parallel to the brachypinacoid, with a pyramidal termination at one end only. When fresh the crystals are transparent and colorless, but on exposure become opaque. The crystal planes are more or less imperfect, and give indistinct signals, when examined on the reflection-goniometer. The orthorhombic character of a number of these crystals was determined by measurements, the best of which

[1] By Mr. Geo. Otis Smith.

are tabulated below. The crystals measured were about 3 by 10 mm.

Orthorhombic : $\breve{a} : \bar{b} : c =$ 0.4164 : 1 : 0.4608.

Forms observed :

$p =$ (111) P ; $b =$ (010) ∞ P $\breve{\infty}$ $m =$ (110) ∞ P.

Angles.	Observed.	Calculated.
$b : m =$ (010) : (110)	*112° 33′ 30″	$\cdots$
$m : p =$ (110) : (111)	*130° 34′ 15″	$\cdots$
$m : p =$ (110) : ($\bar{1}$11)	130° 40′	130° 34′ 15″
$m : m =$ (110) : (1$\bar{1}$0)	134° 52′ 30″	134° 53′

The orthorhombic character was verified by an optical examination, which showed the extinction on 010 to be parallel, and the plane of the optic axes, parallel to 001, with the acute bisectrix normal to 010.

Di-aniline Chlorostannite, $(C_6H_5NH_3)_2SnCl_4$.—After the preparation of the aniline chlorostannite, one molecule of stannous chloride was added to two molecules of aniline chlorostannite first separated from the solution. These were removed, and the mother-liquor concentrated. Crystals of an entirely different appearance now separated. These were removed, dried in the air, and analyzed for tin and chlorine with the following results :

I. 0.2529 gram salt gave 0.0836 gram SnO_2.
II. 0.2753 gram salt gave 0.0914 gram SnO_2.
III. 0.2529 gram salt gave 0.3182 gram AgCl.
IV. 0.2753 gram salt gave 0.3484 gram AgCl.

	Calculated for $(C_6H_5NH_3)_2SnCl_4$.	I.	II.	III.	IV.
Sn	26.52	26.05	26.16	$\cdots$	$\cdots$
Cl	31.58	$\cdots$	$\cdots$	31.11	31.29

The observed properties of this salt are similar to those of the aniline chlorostannite, except that it is very much more soluble. The crystals are transparent when fresh, and very well defined, but the uneven surfaces did not admit of accurate measurement. They belong to the monoclinic system.

Attempts were made to prepare other compounds of stan-

nous chloride and aniline hydrochloride, the two salts having been mixed in all proportions, from four molecules of stannous chloride and one molecule of aniline hydrochloride to one molecule of stannous chloride and four of aniline hydrochloride. No other salts were obtained. When the stannous chloride was in excess, aniline chlorostannite was formed. When the aniline hydrochloride was in excess, di-aniline chlorostannite separated from the solution. When these were removed and the mother-liquors concentrated, either stannous chloride or aniline hydrochloride would separate.

Di-aniline Chlorostannate, $(C_6H_5NH_3)_2SnCl_6 + 3H_2O$.— When molecular quantities of stannic chloride and aniline hydrochloride were dissolved in dilute hydrochloric acid, mixed and boiled, crystals began to form before the liquid cooled down to the temperature of the room. They were very well defined, uniform and in sheaf-like clusters. After standing in the mother-liquor over night, they were removed and dried. In twenty-four hours they became opaque, losing all their water of crystallization. In order to get these crystals again, fresh quantities of stannic chloride and aniline hydrochloride were used. The same sheaf-like clusters were observed. These were removed from the mother-liquor, dried between layers of drying-paper, and at once analyzed. As it was impossible to dry the crystals thoroughly without loss of water of crystallization, the analyses were not very sharp. The following are the best results obtained :

I. 0.1330 gram salt gave 0.0342 gram SnO_2.
II. 0.3489 gram salt gave 0.0898 gram SnO_2.
III. 0.1330 gram salt gave 0.1994 gram AgCl.
IV. 0.1296 gram salt gave 0.1954 gram AgCl.

	Calculated for $(C_6H_5NH_3)_2SnCl_6 + 3H_2O$.	I.	Found. II.	III.	IV.
Sn	20.74	20.26	20.30	....	....
Cl	37.06	....	....	37.08	37.20

Attempts were now made to get the anhydrous crystals mentioned above in a pure form for study. Repeated recrystallizations produced two different kinds of crystals, one kind arranged very closely in tufts, the other comparatively

long and straight. It was impossible to obtain a uniform set. They were at last separated mechanically and analyzed, and found to be of identical composition.

I. 0.2008 gram salt gave 0.0588 gram SnO_2.

II. 0.2904 gram salt gave 0.0850 gram SnO_2.

III. 0.2666 gram salt gave 0.4410 gram AgCl.

IV. 0.1802 gram salt gave 0.2980 gram AgCl.

	Calculated for $(C_6H_5NH_3)_2SnCl_6$.	I.	II.	III.	IV.
			Found.		
Sn	22.89	23.08	23.07	....	....
Cl	40.91	....	....	40.90	40.90

Properties.—It dissolves in water. After standing a longer time than in the case of the stannous compounds the solution becomes turbid. The same turbid appearance occurs when it is dissolved in dilute sulphuric acid. In other respects it closely resembles the stannous compounds. The crystals of this salt are transparent, and change very slowly when in contact with the air. A crystallographic study of these compounds has been made by Hjortdahl.[1]

All attempts to make other compounds of stannic chloride and aniline hydrochloride, by having the one or the other salt in excess, failed.

ORTHOTOLUIDINE SALTS.

Orthotoluidine Chlorostannite, $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.—In studying the compounds formed with the three toluidines, the line of work was similar to that in the case of aniline. Stannous chloride and orthotoluidine hydrochloride were mixed in all proportions, from two molecules stannous chloride and one molecule orthotoluidine hydrochloride to one molecule of stannous chloride and four of orthotoluidine hydrochloride. In each beaker beautiful white opaque crystals separated from the solution. These were taken from the mother-liquor, dried in the air, and analyzed. The mother-liquors were concentrated and crystals were again formed and removed. Only one double salt was obtained. At the one extreme, stannous chloride separated from the solution, and at the other extreme orthotoluidine hydrochloride separated.

[1] *Loc. cit.*

The crystals were analyzed for tin and chlorine with the following results :

I. 0.5107 gram salt gave 0.2267 gram SnO_2.

II. 0.4933 gram salt gave 0.2187 gram SnO_2.

III. 0.1792 gram salt gave 0.2248 gram AgCl.

IV. 0.3837 gram salt gave 0.4813 gram AgCl.

	Calculated for $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.	I.	II.	III.	IV.
				Found.	
Sn	34.87	34.98	34.94	....	....
Cl	31.04	....	....	31.02	31.02

Doubt as to the presence of the half-molecule of water having arisen, the salt was slowly dried at a temperature of about 70°. Owing to the ready decomposition and the volatility of these compounds, not much reliance was placed on this as a general method for the determination of the water. In this case two specimens of the salt were weighed, and heated for about twenty-four hours at 70°. After this a qualitative examination showed that no more water was present.

0.3843 gram salt lost in weight 0.0106 gram, corresponding to 2.75 per cent. H_2O.

0.4345 gram salt lost in weight 0.0117 gram, corresponding to 2.69 per cent. H_2O.

Calculated H_2O for $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$ is 2.62 per cent.

This salt crystallizes in prisms, but no crystals perfect enough for measurement were obtained.

Tri-orthotoluidine Chlorostannate, $(C_7H_7NH_3)_3SnCl_7 + 2H_2O$. —Stannic chloride and orthotoluidine hydrochloride were mixed in molecular proportions and treated in the usual manner. Soon after the solution began to cool, crystals appeared. The simple chlorides were also mixed in all proportions, from two molecules of stannic chloride and one molecule of orthotoluidine hydrochloride to one molecule of stannic chloride and six molecules of orthotoluidine hydrochloride. Crystals appeared in each beaker ; these were removed and purified by recrystallization. Although the mother-liquors were concentrated and new crops of crystals removed, the analyses showed that only one double salt of

stannic chloride and orthotoluidine hydrochloride was formed.

I. 0.3372 gram salt gave 0.0694 gram SnO_2.
II. 0.1378 gram salt gave 0.0286 gram SnO_2.
III. 0.3205 gram salt gave 0.4424 gram AgCl.
IV. 0.3372 gram salt gave 0.4649 gram AgCl.

	Calculated for $(C_7H_7NH_3)_2SnCl_7 + 2H_2O$.	I.	II.	III.	IV.
			Found.		
Sn	16.37	16.22	16.36	....	....
Cl	34.10	....	....	34.13	34.09

METATOLUIDINE SALTS.

Metatoluidine Stannite, $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.—As in the case of the orthotoluidine compounds, stannous chloride and metatoluidine hydrochloride were mixed in different proportions, from a large excess of stannous chloride to a large excess of metatoluidine hydrochloride. In each case beautiful silver-white, opaque crystals separated in very thin leaflets. Analyses showed that these are identical. The results of the determinations of tin and chlorine are as follows:

I. 0.2516 gram salt gave 0.1119 gram SnO_2.
II. 0.2848 gram salt gave 0.1258 gram SnO_2.
III. 0.2848 gram salt gave 0.3581 gram AgCl.
IV. 0.2147 gram salt gave 0.2706 gram AgCl.

	Calculated for $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.	I.	II.	III.	IV.
			Found.		
Sn	34.79	35.05	34.81	....	....
Cl	31.05	....	....	31.09	31.12

The general properties of this salt are similar to those of the corresponding aniline compound. It changes over into the stannic condition when allowed to stand in hydrochloric-acid solution for a few weeks, the solution changing to a dark color. Owing to lack of time a quantitative study of this reaction was not made.

Di-metatoluidine Chlorostannate, $(C_7H_7NH_3)_2SnCl_6 + H_2O$. —This salt has a very strong crystallizing force, and is easily obtained by mixing stannic chloride and metatoluidine hydrochloride in any proportion. If the toluidine hydrochloride is in great excess, the crystals that separate from the solution

will be mixtures of it and the di-toluidine chlorostannate. These crystals were purified by recrystallization, removed from the mother-liquor, and dried in the air. Analyses for tin and chlorine gave the following results:

I. 0.2434 gram salt gave 0.0650 gram SnO_2.
II. 0.2693 gram salt gave 0.0721 gram SnO_2.
III. 0.2434 gram salt gave 0.3689 gram AgCl.
IV. 0.2693 gram salt gave 0.4091 gram AgCl.

	Calculated for $(C_7H_7NH_2)_2SnCl_6 + H_2O$.	I.	II.	III.	IV.
			Found.		
Sn	21.04	21.06	21.10	....	....
Cl	37.59	....	....	37.48	37.56

Crystallography of the Salt.[1]—The crystals of di-metatoluidine chlorostannate are tabular, parallel to the basal pinacoid. They are transparent and only faintly tinged with red, often showing an hour-glass arrangement with different shades of color.

Only one of the crystals gave distinct signals, when examined on the reflecting-goniometer, although good crystal-faces were developed on most of the crystals. The measurements showed the crystal to be monoclinic, and this result was verified by an optical examination.

Five forms were determined on this crystal, and another crystal showed the clino-pinacoid also to be present, although measurements could not be made. Cleavages parallel to the basal pinacoid and clino-pinacoid were observed.
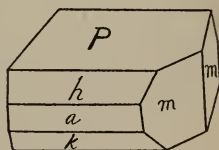
The forms determined, the angles observed and calculated, and the axial constants determined are tabulated below:

$$\text{Monoclinic}: \check{a} : \bar{b} : \acute{c} = 1.924 : 1 : 1.463$$
$$\beta = 86°\ 3'$$

Forms: $P = \{\ 001\ \}\ oP$
$h = \{\ 101\ \}\ -P\bar{\infty}$
$k = \{\ 10\bar{1}\ \}\ +P\bar{\infty}$
$a = \{\ 100\ \}\ \infty\,P\bar{\infty}$
$m = \{\ 120\ \}\ \infty\,\acute{P}2$

[1] By Mr. Geo. Otis Smith.

Angles.	Observed.	Calculated.
$P:a=(001):(\bar{1}00)$	*86° 38′	...
$P:a=(001):(100)$	93° 6′	93° 22′
$m:m=(120):(\bar{1}20)$	*38° 34′	...
$m:m=(\bar{1}20):(1\bar{2}0)$	38° 34′	38° 34′
$P:h=(001):(\bar{1}01)$	143° 54′	144° 3′
$P:k=(001):(\bar{1}01)$	*141° 36′	...

PARATOLUIDINE SALTS.

Paratoluidine Chlorostannite, $C_7H_7NH_8SnCl_8 + \frac{1}{2}H_2O$.—
Stannous chloride and paratoluidine hydrochloride were
mixed in all proportions, from three molecules of stannous
chloride and one molecule of paratoluidine hydrochloride to
one molecule of stannous chloride and four of paratoluidine
hydrochloride. In each beaker crystals were very easily
obtained. These all appeared to be identical, but analyses
showed that the simple chlorides unite in two different pro-
portions. When the simple chlorides were mixed in molec-
ular proportions, and when the stannous chloride was in
excess, paratoluidine chlorostannite was formed. The crys-
tals were removed and dried in the usual manner. Analyses
for tin and chlorine gave the following results:

I. 0.2421 gram salt gave 0.1071 gram SnO_2.
II. 0.1901 gram salt gave 0.0839 gram SnO_2.
III. 0.2814 gram salt gave 0.3498 gram AgCl.
IV. 0.2596 gram salt gave 0.3235 gram AgCl.

	Calculated for $C_7H_7NH_8SnCl_3 + \frac{1}{2}H_2O$.	Found.			
		I.	II.	III.	IV.
Sn	34.79	34.86	34.78	....	....
Cl	31.05	....	....	30.74	30.81

This salt is very well defined crystallographically. The
crystals were of a light-yellow color, not perfect enough for
measurement.

The properties of this salt are, in general, similar to those of
the corresponding aniline salt. After standing a few weeks
in dilute hydrochloric-acid solution, it changes color and
passes over into the stannic condition.

Di-paratoluidine Chlorostannite, $(C_7H_7NH_8)_2SnCl_4$.—When

one molecule of stannous chloride was added to two molecules of paratoluidine hydrochloride, and when the latter was in excess of this proportion, crystals were formed which resembled the paratoluidine chlorostannite. These were analyzed with the following results:

I. 0.2522 gram salt gave 0.0784 gram SnO_2.

II. 0.2692 gram salt gave 0.3239 gram AgCl.

III. 0.3026 gram salt gave 0.3659 gram AgCl.

	Calculated for $(C_7H_7NH_2)_2SnCl_4$.	I.	Found. II.	III.
Sn	24.96	24.50	....	....
Cl	29.72	....	29.75	29.90

This salt is much more soluble than the paratoluidine chlorostannite. The mother-liquors were concentrated and new crops of crystals were obtained. Analysis showed that these were either one of the double salts above described or paratoluidine hydrochloride. We therefore concluded that stannous chloride and paratoluidine hydrochloride form only two double salts.

Di-paratoluidine Chlorostannate, $(C_7H_7NH_2)_2SnCl_6 + H_2O$. —The stannic chloride and paratoluidine hydrochloride were mixed in all proportions, from two molecules of stannic chloride and one molecule of paratoluidine hydrochloride to one molecule of stannic chloride and four of paratoluidine hydrochloride. The compound formed had a stronger crystallizing force than any other salt of this series. Analyses showed that only one double salt was formed by these two chlorides.

I. 0.4970 gram salt gave 0.1309 gram SnO_2.

II. 0.5205 gram salt gave 0.1385 gram SnO_2.

III. 0.5205 gram salt gave 0.7929 gram AgCl.

IV. 0.3478 gram salt gave 0.5292 gram AgCl.

	Calculated for $(C_7H_7NH_2)_2SnCl_6 + H_2O$.	I.	Found. II.	III.	IV.
Sn	21.04	20.76	20.97	....	....
Cl	37.59	....	....	37.65	37.61

A crystallographic study of this salt has been made by Hjortdahl.[1] The crystals are transparent, of a light-yellow

[1] *Loc. cit.*

color. They effloresce slowly when in contact with the air.

All efforts made to obtain other salts of stannic chloride and paratoluidine hydrochloride met with failure.

Whether other double salts of the chlorides of tin with the chlorides of aniline and the toluidines exist or not it is impossible to say, but it can be said that careful attempts, which were unsuccessful, were made to prepare other salts by the method already described. The properties and solubilities of these compounds were not as thoroughly studied as desired on account of lack of time. Another interesting fact that was not thoroughly investigated is the change of the stannous salts to the stannic condition when allowed to stand several weeks in dilute hydrochloric-acid solution. In the case of aniline, however, it was shown that the aniline chlorostannite changed into di-aniline chlorostannate. After standing four months, the color of the solution had changed through red to almost black, a change similar to that which aniline alone undergoes.

ON DOUBLE HALIDES OF ZINC WITH ANILINE AND THE TOLUIDINES.

By Daniel Base.[1]

In the continuation of the investigation of double halides containing organic bases, it seemed desirable to study those of zinc with aniline and the toluidines, an account of which is given in this paper. As the halides of the organic bases are closely related to the ammonium halides, and as a number of zinc ammonium double chlorides are recorded in the literature, some of which do not conform to the law and the authority for which might be questioned, it seemed proper, at the same time, to make a study of these compounds. This work will be spoken of in the latter part of this paper.

All the double salts of zinc with inorganic as well as organic halides, that have been recorded in the journals up to the present, have been collected and tabulated. For the sake

of completeness, it is thought well to give a list of these salts with the references.

Double Chlorides.

$ZnCl_2.2NH_4Cl.H_2O$.   Geiger's and Liebig's Mag., **36**, 43 : Schindler.

$ZnCl_2.2NH_4Cl.H_2O$.   Ann. Chem. (Liebig), **66**, 280 : Hautz.

$ZnCl_2.NH_4Cl.2H_2O$.   *Ibid*, **66**, 280 : Hautz.

$ZnCl_2.2NH_4Cl$.   Ann. der Phys. Pogg., **94**, 507 : Rammelsberg.

$ZnCl_2.NH_4Cl$.   Ann. des Mines (5), **12**, 1 : Marignac.

$ZnCl_2.3NH_4Cl$.   Ann. des Mines (5), **12**, 1 : Marignac.

$ZnCl_2.3NH_4Cl.H_2O$.   Ann. chim. phys. [6], **11**, 308 : Berthelot and André.

$ZnCl_2.6NH_4Cl.\frac{2}{3}H_2O$.   *Loc. cit.* : Berthelot and André.

$ZnCl_2.4NH_4Cl$.   Bull. Soc. Chim. (1861), 51 : Dehérain.

$ZnCl_2.2KCl$.   Ann. der Phys. Pogg., **94**, 507 : Rammelsberg.

$ZnCl_2.2HCl$.   Ann. des Mines [5], **12**, 1 : Marignac.

$ZnCl_2.2NaCl.3H_2O$.   *Ibid* [5], **12**, 1 : Marignac.

$ZnCl_2.BaCl_2.4H_2O$.   Chem. News, **27**, 271 ; and **28**, 186: G. Warner.

$ZnCl_2.MgCl_2.6H_2O$.   *Ibid*.

$ZnCl_2.3CsCl$.   Am. J. Sci. [3], **46**, 425 : Wells and Campbell.

$ZnCl_2.2CsCl$.   *Loc. cit.* : Wells and Campbell.

$ZnCl_2.PtCl_4.6H_2O$.   Jour. prakt. Chem. [2], **15**, 277 : Nilson.

$ZnCl_2.PtCl_4.6H_2O$.   Jsb. Chem. (1870), 393 : Topsoë.

$ZnCl_2.PdCl_4.6H_2O$.   *Ibid*. (1870), 393 : Topsoë.

$ZnCl_2.2AuCl_3.8H_2O$.   Wien. Akad. Ber. (2 Abth.), **69**, 266 : Topsoë.

$ZnCl_2.2AuCl_3.12H_2O$.   Ann. der Phys. (Pogg.), **17**, 261; **33**, 64 : Von Bonsdorff.

$ZnCl_2.2AuCl_3$.   *Ibid*, **17**, 261 ; **33**, 64 : Von Bonsdorff.

Double Chlorides with Organic Constituents.

$ZnCl_2.2C_9H_{14}N_2.HCl$(Cyanconiïne).   J. prakt. Chem. [2], **22**, 281 : E. v. Meyer.

ZnCl$_2$.2C$_9$H$_7$N.HCl(Quinoline).   Ber. d. chem. Ges., **15**, 645 : Wallach.

ZnCl$_2$.2(Tetraethyldiamidotriphenylcarbinol.2HCl).   Ann. Chem. (Liebig), **217**, 223 : Döbner.

ZnCl$_2$.(*p*-Amido-*o*-imidophenylurea).   Ber. d. chem. Ges., **17**, 2632 : Hager.

ZnCl$_2$.(Quinine.2HCl).2H$_2$O.   *Ibid*, **18**, 1225 : Comstock and Königs.

ZnCl$_2$.2(Papaverin.HCl).   Monatshefte, **6**, 667 : Gold-schmidt.

ZnCl$_2$.(β-Picolin.HCl).   Ber. d. chem. Ges., **18**, 3091 : Ad. Hesekiel.

ZnCl$_2$.2(α-γ-Dimethylquinoline.HCl).   Jour. prakt. Chem. [2], **33**, 393.   C. Beyer.

ZnI$_2$.2(Papaverin.HCl).   Monatshefte, **7**, 506 : Jahoda.

ZnCl$_2$.2(Ethenyltriamidonaphthalene.HCl).   J. Chem. Soc., **51**, 607 : Meldola and Streatfield.

ZnCl$_2$.(Isocinchonine.2HCl).   Ber. d. chem. Ges., **20**, 2510 : Comstock and Königs.

ZnCl$_2$.2C$_5$H$_5$N.HCl.   *Ibid*, **21**, 1578 : Lang.

ZnCl$_2$.(Dipyridin.2HCl).   J. Chem. Soc. [2], **7**, 411 : An-derson.

Double Bromides.

ZnBr$_2$.2CsBr.   Am. J. Sci. [3], **46**, 425 : Wells and Camp-bell.

ZnBr$_2$.3CsBr.   *Loc. cit.* : Wells and Campbell.

ZnBr$_2$.2NH$_4$Br.   Jsb. Chem. (1860), 17 : Boedeker.

3ZnBr$_2$.2DiBr$_3$.36H$_2$O.   Ann. Chem. (Liebig), **191**, 342 : Frerichs and Smith.

3ZnBr$_2$.DiBr$_3$.12H$_2$O.   Bull. Soc. Chim. [2], **43**, 361 : P. T. Cleve.

3ZnBr$_2$.2LaBr$_3$.39H$_2$O.   Ann. Chem. (Liebig), **191**, 357 : Frerichs and Smith.

ZnBr$_2$.PtBr$_4$.12H$_2$O.   N. Archiv. ph. nat., **35**, 58 : Topsoë.

Double Iodides.

ZnI$_2$.2NH$_4$I.   Ann. der Phys. (Pogg.), **43**, 665 : Rammels-berg.

ZnI$_2$.KI.   *Loc. cit.* : Rammelsberg.

$ZnI_2.2NaI.3H_2O$. *Loc. cit.*: Rammelsberg.

$2ZnI_2BaI_2$. *Loc. cit.*: Rammelsberg.

$ZnI.As(CH_3)_4I$ (old formula). Compt. rend., **49**, 87 : Cahours.

$ZnI.As(C_2H_5)_4I$ (old formula). *Loc. cit.*: Cahours.

$ZnI.P(C_2H_5)_4I$ (old formula). Ann. chim. phys. [3], **62**, 333 : Cahours.

$ZnI.P(C_2H_5)3HI$ (old formula). *Loc. cit.*: Cahours.

$3ZnI_2.2DiI_2.24H_2O$. Ann. Chim. (Liebig), **191**, 343 : Frerichs and Smith.

$3ZnI_2.2LaI_2.27H_2O$. *Loc. cit.*: Frerichs and Smith.

$ZnI_2PtI_4.9H_2O$. N. Archiv. ph. nat., **38**, 297 : Topsoë.

$ZnI_2.2CsI$. Am. J. Sci. [3], **46**, 425 : Wells and Walden.

$ZnI_2.3CsI$. *Loc. cit.*: Wells and Walden.

Double Fluorides.

$ZnFl.SiFl_2.6HO$ (old formula). Ann. des Mines [5], **15**, 221 : Marignac.

$ZnFl_2.TaFl_5.7H_2O$. Ann. chim. phys. [4], **19**, 274 : Marignac.

$ZnFl_2.SnFl_4.6H_2O$. Ann. des Mines [5], **15**, 221 : Marignac.

$ZnFl_2.2KFl$. Ann. der. Phys. (Pogg.), **1**, 26 : Berzelius.

$ZnFl_2.Al_2Fl_6$. *Loc. cit.*: Berzelius.

$ZnFl_2.KFl$. Ber. d. chem. Ges., **19**, 896 : Wagner.

$ZnFl_2.NaFl$. *Loc. cit.*: Wagner.

$ZnFl_2.2NH_4Fl.2H_2O$. *Loc. cit.*: Wagner.

$ZnFl_2.2BFl_3$. *Loc. cit.*: Wagner.

$2ZnFl_2.Mn_2Fl_6.8H_2O$. J. prakt. Chem. [2], **34**, 41 : Christensen.

All of the salts included in the above list, with one exception, are in harmony with the law of composition of double halides pointed out by Professor Remsen.[1] The exception is the ammonium compound of the formula $ZnCl_2.6NH_4Cl.\frac{2}{3}H_2O$ described by Berthelot and André. It will, however, be shown in this article that this salt cannot be obtained.

Methods of Analysis.—The salts were analyzed for zinc, halogen, and water of crystallization when present. Zinc was

[1] This JOURNAL, **11**, 296.

precipitated as carbonate and weighed as oxide. The organic bases had no solvent action on the zinc carbonate, as ammonia has when present in the solution.

Chlorine was determined gravimetrically or volumetrically by Volhard's method.

Compounds Described.

Dianiline chlorozincate, $ZnCl_2.2C_6H_5.NH_3Cl.H_2O$.

Trianiline chlorozincate, $ZnCl_2.3C_6H_5.NH_3Cl.2H_2O$.

Diorthotoluidine chlorozincate, $ZnCl_2.2C_6H_4\begin{smallmatrix}CH_3\\NH_3Cl\text{-}o\end{smallmatrix}$ $.2H_2O$.

Dimetatoluidine chlorozincate, $ZnCl_2.2C_6H_4\begin{smallmatrix}CH_3\\NH_3Cl\text{-}m\end{smallmatrix}$.

Trimetatoluidine chlorozincate, $ZnCl_2.C_6H_4\begin{smallmatrix}CH_3\\NH_3Cl\text{-}m\end{smallmatrix}$.

Diparatoluidine chlorozincate, $ZnCl_2.2C_6H_4\begin{smallmatrix}CH_3\\NH_3Cl\text{-}p\end{smallmatrix}$.

Triparatoluidine chlorozincate, $ZnCl_2.3C_6H_4\begin{smallmatrix}CH_3\\NH_3Cl\text{-}p\end{smallmatrix}$.

Dianiline bromozincate, $ZnBr_2.2C_6H_5NH_3BrH_2O$.

Diorthotoluidine bromozincate, $ZnBr_2.2C_6H_4\begin{smallmatrix}CH_3.H_2O\\NH_3Br\text{-}o\end{smallmatrix}$.

Dimetatoluidine bromozincate,

$$ZnBr_2.2C_6H_4\begin{smallmatrix}CH_3\\NH_3Br.2H_2O\text{-}m\end{smallmatrix}.$$
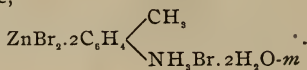
Trimetatoluidine bromozincate, $ZnBr_2.3C_6H_4\begin{smallmatrix}CH_3\\NH_3Br\text{-}m\end{smallmatrix}$.

Diparatoluidine bromozincate, $ZnBr_2.2C_6H_4\begin{smallmatrix}CH_3\\NH_3Br.H_2O\text{-}p\end{smallmatrix}$.

Diammonium chlorozincate, $ZnCl_2.2NH_4Cl$.

Triammonium chlorozincate, $SnCl_2.3NH_4Cl$.

Double Chlorides.

Dianiline Chlorozincate, $ZnCl_2.2C_6H_5NH_3Cl.H_2O$. — This

salt was made by H. Vohl[1], in 1865, in an indirect way. In an article, "On the Compounds of Zinc Chloride with Aniline and the Application of the Same in the Arts," Vohl describes the preparation of the salt $ZnCl_2.2C_6H_5NH_2$. According to him it forms shining white needles, which can be crystallized from alcohol, but are decomposed by water. In dilute hydrochloric acid the compound is easily soluble and yields a salt crystallizing in large colorless columnar crystals and plates, which become colored violet-blue in contact with the air. This salt is easily soluble in alcohol and water. It contains water of crystallization, which escapes completely at 105° C. Heated more strongly it melts, vapors of aniline hydrochloride are formed, while zinc chloride remains behind, which takes on a violet-blue color.

This description of the double salt by Vohl was found to be correct, and his analyses were good, showing the salt to have the above formula. His object in making the double salts was to prepare aniline dyes in accordance with the method in use at that time. By mixing the double salt with an oxidizing agent, as mercurous nitrate, and heating, magenta was formed. Vohl made no systematic study of double salts nor had he any idea of getting more than one aniline salt, and therefore a repetition of the work in a thorough manner was necessary, especially as the object now is to get evidence for or against the law of composition of double salts. My work has shown that there are two double aniline salts, one being identical with that described by Vohl.

When zinc chloride and aniline hydrochloride are mixed so that the number of molecules of the former to that of the latter bear these relations, 3 : 1, 2 : 1, 1 : 1, 1 : 2, dianiline chlorozincate is formed in every case. It seems to make no difference whether the solutions are heated or not, or whether they are neutral or made acid. The solutions soon change color to a reddish-brown, or greenish color, even when mixed in the cold. The ease with which they become colored varies with the proportion of aniline hydrochloride present. Alcoholic solutions color extremely rapidly. On standing, a flocculent greenish material is formed in the solutions. The

[1] Ding. poly. J., **175**, 211.

shape of the crystals varies with conditions. The most frequent form is the plates spoken of by Vohl, which belong to the triclinic system. The salt is easily purified by recrystallization from water. When pure it does not change color readily in the air. It loses all its water in the sulphuric-acid desiccator, the weight remaining constant after transferring to an air-bath and heating to 100° C. It is extremely soluble in methyl alcohol, so much so that it cannot be recrystallized from this. It is less soluble in ethyl alcohol.

0.459 gram salt gave 0.0904 gram ZnO and 0.6365 gram AgCl.

0.3912 gram salt gave 0.0772 gram ZnO and 0.5408 gram AgCl.

0.4405 gram salt lost 0.0191 gram water.

	Calculated for $ZnCl_2.2C_6H_5NH_3Cl.H_2O$.	I.	Found. II.	III.
Zn	15.77	15.81	15.82	....
Cl	34.32	34.3	34.18	....
H_2O	4.35	....	....	4.34

Trianiline Chlorozincate, $ZnCl_2.3C_6H_5NH_3Cl.2H_2O$.—When zinc chloride and aniline hydrochloride are brought together in water solution so that the molecular proportions of the former to the latter are as 1 : 3, 1 : 4, 1 : 6, trianiline chlorozincate is formed. The 1 : 3 mixture yields the dianiline salt also, which can easily be separated from the trianiline salt on account of its totally different form. The solutions soon become deeply colored, but the crystals are colored only a little, and by washing with water are pure enough for analysis. When pure they are colorless. The salt is more soluble in water and alcohol than the dianiline salt. It is stable in the air, but on long exposure it turns green. It loses all its water in the sulphuric-acid desiccator, and can be heated in the air-bath to 100° without decomposition. It forms long prisms apparently of the orthorhombic system. The forms are unit prism and macro prism.

0.3538 gram salt gave 0.051 gram ZnO and 0.4536 gram AgCl.

0.2875 gram salt gave 0.042 gram ZnO and 0.369 gram AgCl.

0.2194 gram salt lost 0.0143 gram H_2O.

	Calculated for $ZnCl_2.3C_6H_5NH_3Cl.2H_2O.$	I.	Found. II.	III.
Zn	11.62	11.57	11.74	....
Cl	31.58	31.7	31.75	....
H_2O	6.41	....	....	6.52

Diorthotoluidine Chlorozincate, $ZnCl_2.2C_6H_4\Big\langle {CH_3.H_2O \atop NH_3Cl}$.—

This compound was prepared in 1865 by Gräfinghoff,[1] who made a study of the action of the toluidines (ortho and para) on zinc chloride. He was led to this study by the work of Vohl, already referred to. His object was the same as Vohl's, that is, the preparation of compounds of zinc chloride with toluidine for technical application in the preparation of dyes. On treating the toluidine compound with hydrochloric acid, drying on the water-bath, and taking up with alcohol, he says he obtained the salt $ZnCl.2C_7H_9N.HCl$. This salt, he says, can also be prepared directly from zinc chloride and toluidine hydrochloride, and when obtained from water solution contains water of crystallization, but when obtained from alcohol it contains no water. He says further, " to avoid the objection that the existence of these salts was shown only for the liquid toluidine, toluidine was prepared from pure toluene from tolu balsam, which, according to Muspratt and Hofmann, was solid. Salts were formed in the same manner and analyzed, and their identity with those from the liquid toluidine shown. They agreed in solubility and physical properties perfectly with the latter.

Gräfinghoff's object evidently was not to make a systematic study of double halides.

Bibanow[2] also says he obtained from a mixture of ortho-toluidine hydrochloride and a concentrated solution of zinc chloride, by cooling down to —5°, a salt of the composition $ZnCl_2.2C_6H_4\Big\langle {CH_3 \atop NH_3Cl}$, having no water of crystallization and forming colorless concentrically grouped plates.

Zinc chloride and orthotoluidine hydrochloride were brought together in aqueous solution in the molecular proportions 3:1,

[1] J. prakt. Chem., **95**, 221.　　　　[2] Mon. scient. (3), **4**, 925.

2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4. In the last case the toluidine hydrochloride separated out first. The solutions were heated to boiling, and it mattered not whether they were made acid or not. They did not change color nearly so rapidly as the solutions containing zinc chloride and aniline chloride, and they deposited very little of the green flocculent material.

Analysis showed that only one salt was obtained from all these mixtures—the same as that obtained by Gräfinghoff. The salt is colorless when pure, but gradually becomes colored when exposed to the air. It gives off water and takes it up again, according to the temperature and hygroscopic state of the atmosphere. Solutions of the salt easily become supersaturated, and, in strong solutions, the salt crystallizes out in long, concentrically grouped plates, as described by Bibanow. The plates are striated, so that they have a sort of hour-glass appearance. They lose all their water over sulphuric acid, and can be heated in the air-bath to 120° without decomposing. When heated high enough, the salt melts to a brown liquid from which toluidine hydrochloride sublimes. As the salt loses water easily, it must be pressed between filter-paper, powdered, and not allowed to lie long in the air before analysis.

0.2775 gram salt lost 0.0024 gram water.

0.2021 gram salt gave 0.0359 gram ZnO and 0.2539 gram AgCl.

0.331 gram salt gave 0.0595 gram ZnO and 0.4171 gram AgCl.

	Calculated for $ZnCl_2.2C_6H_4\genfrac{}{}{0pt}{}{CH_3\ 2H_2O}{NH_3Cl}$	I.	Found. II.	III.
Zn	14.42	....	14.26	14.33
Cl	30.86	....	31.06	31.16
H_2O	7.83	8.07	....	....

Dimetatoluidine Chlorozincate, $ZnCl_2.2C_6H_4\genfrac{}{}{0pt}{}{CH_3}{NH_2Cl}$.—This

salt is formed when the constituents are brought together in the molecular proportions 3 : 1, 2 : 1. It forms fine, silken needles, which are extremely soluble in water. They cannot be washed, but must be sucked dry on the filter-pump and

pressed between filter-paper. Owing to the nature of the crystals and their great solubility, it is very difficult to get a specimen of the salt pure enough to give sharp analytical results. The results are not as good as could be desired, but they are close enough to show that the compound has the formula given above.

0.0941 gram salt gave 0.0187 gram ZnO and 0.03187 gram Cl.

0.1917 gram salt gave 0.0377 gram ZnO and 0.2568 gram AgCl.

	Calculated for $ZnCl_2.2C_6H_4\genfrac{}{}{0pt}{}{CH_3}{NH_3Cl}$.	I.	Found.	II.
Zn	15.42	15.95		15.8
Cl	33.48	33.87		33.13

These results were from different specimens.

Trimetatoluidine Chlorozincate, $ZnCl_2.3C_6H_4\genfrac{}{}{0pt}{}{CH_3}{NH_3Cl}$.—Mixtures of zinc chloride and metatoluidine hydrochloride were made in aqueous solution in the proportions of 1 : 1, 1 : 2, 1 : 3, 1 : 4. All these gave the same double salt, the trimetatoluidine chlorozincate. The solutions soon assume a purple color, and the crystals are nearly always colored. When pure, they are colorless. The salt crystallizes in fine needles, which grow in radiating tufts and are not as soluble as the ditoluidine salts, but still are too soluble to be washed with water, and must be sucked dry and pressed between drying-paper. In this way they are obtained in good condition for analysis.

0.1394 gram salt gave 0.0201 gram ZnO and 0.1751 gram AgCl.

0.1929 gram salt gave 0.028 gram ZnO and 0.2426 gram AgCl.

0.2225 gram salt gave 0.0316 gram ZnO and 0.278 gram AgCl.

	Calculated for $ZnCl_2.3C_6H_4\genfrac{}{}{0pt}{}{CH_3}{NH_3.Cl}$.	I.	Found. II.	III.
Zn	11.5	11.57	11.65	11.4
Cl	31.24	31.06	31.14	30.92

Diparatoluidine Chlorozincate, $ZnCl_2.2C_6H_4\underset{NH_2Cl}{\overset{CH_3}{<}}$.—This

salt was referred to under the corresponding orthotoluidine
salt. Gräfinghoff said he prepared this at the same time that
he made the ortho salt. He did not give any analysis nor
did he state whether only one salt could be formed or more
than one. There are two para salts, while only one ortho
salt could be made.

Diparatoluidine chlorozincate is formed when zinc chloride
and toluidine hydrochloride are mixed in the proportions 3 : 1,
2 : 1, 1 : 1, 1 : 2, 1 : 3. The solutions were heated to boiling
and made slightly acid. The salt crystallizes in colorless
plates, which form a matted mass.

The solutions color very slowly. They cannot be purified
by boiling with boneblack as they become colored more, to a
deep purple. The crystals have various forms, sometimes
triangular plates, sometimes triangular plates with the angles
truncated.

The salt is easily soluble in cold water. It is stable in the
air, and does not change color.

0.2567 gram salt gave 0.0489 gram ZnO and 0.3482 gram
AgCl.

0.2743 gram salt gave 0.0524 gram ZnO and 0.3709 gram
AgCl.

	Calculated for $ZnCl_2.2C_6H_4\underset{NH_2Cl}{\overset{CH_3}{<}}$.	Found. I.	II.
Zn	15.42	15.3	15.37
Cl	33.48	33.54	33.44

Triparatoluidine Chlorozincate, $ZnCl_2.3C_6H_4\underset{NH_2Cl}{\overset{CH_3}{<}}$.—This

salt is formed when zinc chloride and paratoluidine hydro-
chloride are brought together in water solutions in the pro-
portions 1 : 3, 1 : 4. The 1 : 4 mixture deposits the organic
halide first. Sometimes the ditoluidine salt is formed in the
1 : 3 mixture. There is this tendency at low temperatures.
At a slightly elevated temperature only the 1 : 3 salt is formed.

The compound crystallizes well, apparently in the triclinic

system, and resembles albite crystals in outline. The forms
are oP, $\bar{P}'\infty$, $\infty_{1}'P$, $\infty_{1}'P$, $\check{\infty}P\infty$.

0.191 gram salt gave 0.0263 gram ZnO and 0.2406 gram
AgCl.

0.2483 gram salt gave 0.0354 gram ZnO and 0.315 gram
AgCl.

	Calculated for $ZnCl_2.3C_6H_4\genfrac{}{}{0pt}{}{CH_3}{NH_3Cl}$.	Found.	
		I.	II.
Zn	11.50	11.05	11.45
Cl	31.24	31.15	31.37

Double Bromides.

Dianiline Bromozincate, $ZnBr_2.2C_6H_5NH_3Br.H_2O.$—Aniline
hydrobromide behaves a little differently from the correspond-
ing chloride, in that it separates out as such from mixtures in
which the proportion of aniline hydrobromide to zinc bromide
is greater than 2 : 1. A 3 : 1 mixture could not be made as
in the case of the chloride. Addition of hydrobromic acid
caused a still greater separation of the organic halide. Only
one double salt could be obtained from all the different mix-
tures. It seemed to be best formed in a 1 : 1 solution. Some-
times a solution of one molecule of zinc bromide to two mole-
cules of organic halide would deposit the organic halide along
with the double salt. The salt crystallizes in thick prismatic
plates resembling those of the corresponding double chloride,
and probably belonging to the same system.

The solutions remain colorless, differing again in this
respect from those of the corresponding chloride. The salt
cannot be recrystallized from water, as aniline hydrobromide
separates out. It is easily soluble in cold water. It loses its
water when heated and does not decompose at 110°.

0.2452 gram salt gave 0.0345 gram ZnO and 0.3112 gram
AgBr.

0.2249 gram salt gave 0.0318 gram ZnO.

0.2609 gram salt gave 0.3315 gram AgBr.

0.1758 gram salt lost 0.0052 gram H_2O.

	Calculated for $ZnBr_2.2C_6H_5NH_3Br.H_2O$.	I.	II.	III.	IV.
			Found.		
Zn	11.02	11.30	11.35	....	....
Br	54.19	54.00	....	54.06	....
H_2O	3.05	....	....	....	3.24

Diorthotoluidine Bromozincate, $ZnBr_2 2C_6H_4 \begin{cases} CH_3 . H_2O \\ NH_4Br \end{cases}$.—
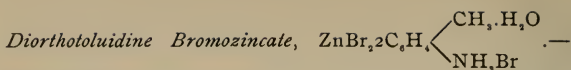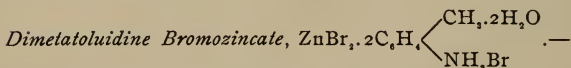
Orthotoluidine hydrobromide is like the chloride in its be-
havior towards zinc bromide ; that is, it does not separate out
as such from mixtures in which it is present in excess, as the
aniline hydrobromide does.   Mixtures were made in many
proportions, but only one salt could be obtained.   The solu-
tions change color slowly.   The salt forms large colorless
prismatic plates, which can be recrystallized from water.   It
can be heated in the air-bath to 120° without decomposition,
and when heated to 150° it begins to melt to a blue liquid, giv-
ing off vapors of toluidine hydrobromide.   The salt is readily
soluble in cold water.

0.2564 gram salt gave 0.0339 gram ZnO and 0.31 gram
AgBr.

0.6305 gram salt gave 0.852 gram ZnO and 0.7963 gram
AgBr.

0.3802 gram salt lost 0.0117 gram water.

	Calculated for $ZnBr_2 . 2C_6H_4 \begin{cases} CH_3 . H_2O \\ NH_3Br. \end{cases}$	I.	Found. II.	III.
Zn	10.52	10.56	10.82	....
Br	51.7	51.45	51.82	....
H_2O	2.9	....	....	3.08

Dimetatoluidine Bromozincate, $ZnBr_2 . 2C_6H_4 \begin{cases} CH_3 . 2H_2O \\ NH_3Br \end{cases}$.—

This salt is formed in solutions which contain zinc bromide in
excess, that is, in 3 : 1, 2 : 1, 1 : 1 solutions.   The salt is with
difficulty obtained in pure condition, as there is a strong ten-
dency to the formation of a trituoluidine salt, to be described
presently.

Sometimes in these mixtures one crop will be the ditolui-
dine salt, the next crop a tritoluidine salt, and the third a di-
toluidine salt again.   The ditoluidine salt forms long, thick,
prismatic bars.   The solution soon becomes colored, and the
crystals are nearly always more or less colored.

The compound loses its water in the air-bath and can be
heated above 100° without decomposing.

0.2647 gram salt gave 0.0336 gram ZnO and 0.3128 gram $AgBr$.

0.2184 gram salt gave 0.0275 gram ZnO and 0.2581 gram $AgBr$.

0.2647 gram salt lost 0.0147 gram water.

	Calculated for $ZnBr_2.2C_6H_4{<}^{CH_3.2H_2O}_{NH_3Br}$	I.	Found. II.	III.
Zn	10.23	10.28	10.11	....
Br	50.20	50.27	50.28	....
H_2O	5.64	....	....	5.59

Trimetatoluidine Bromozincate, $ZnBr.3C_6H_4{<}^{CH_3}_{NH_3Br}$.—Of
the two metatoluidine double salts this one is the more easily
formed, being produced in solutions containing an excess of
zinc bromide as well as in those which the toluidine hydro-
bromide is in excess. It crystallizes in long needles or prisms,
for the most part colored purple. By pressing between filter-
paper they are fit for analysis.

0.2291 gram salt gave 0.0237 gram ZnO and 0.11575 gram
Br.

0.2663 gram salt gave 0.0289 gram ZnO and 0.1346 gram
Br.

	Calculated for $ZnBr_2.3C_6H_4{<}^{CH_3}_{NH_3Br}$	I.	Found. II.
Zn	8.26	8.30	8.47
Br	50.71	50.52	50.54

This salt is much less soluble in cold water than the cor-
responding chlorine salt. It was impossible to wash the lat-
ter without dissolving the crop of crystals, while the former
can be washed clean on the filter-pump.

Diparatoluidine Bromozincate, $ZnBr_2.2C_6H_4{<}^{CH_3}_{NH_3Br}$.—When
solutions of zinc bromide and paratoluidine hydrobromide are
made in the proportions of 1 : 1, 1 : 2, 1 : 3, the paratoluidine
hydrobromide crystallizes out without forming a double salt.
Addition of hydrobromic acid causes more of the organic
halide to separate out. In this respect the behavior is like

that of aniline hydrobromide. Mixtures containing zinc bromide in excess, for example 2 : 1, 3 : 1, yield a double salt, crystallizing in large, thin, shining, colorless leaves. These were filtered off, sucked dry, and pressed between filter-paper. When washed with water the crystals become opaque at once, evidently being decomposed. When an effort is made to recrystallize the salt from water, it is broken down, yielding crystals of paratoluidine hydrobromide. The salt is stable in the air and does not change color.

0.2122 gram salt gave 0.0283 gram ZnO.

0.1495 gram salt gave 0.1826 gram AgBr.

0.255 gram salt gave 0.0345 gram ZnO and 0.3107 gram AgBr.

0.2302 gram salt lost 0.0072 gram water.

	Calculated for $ZnBr_2.2C_6H_4{<}^{CH_3.H_2O}_{NH_3Br}$	I.	II.	III.	IV.
			Found.		
Zn	10.52	10.71	....	10.85	....
Br	51.70	....	51.97	51.84	....
H$_2$O	2.9	....	....	....	3.12

Double Ammonium Zinc Chlorides.

As was stated at the beginning of this paper, the close relationship between ammonia and the organic bases made it desirable to investigate the double zinc ammonium chlorides, along with those of the organic bases, especially since a number of them are recorded, in regard to the existence of some of which a doubt may fairly be entertained. The following salts are recorded:

1. $ZnCl_2.2NH_4Cl.H_2O$. Schindler, Geiger's and Liebig's Mag., **36**, 43 ; Hautz, Ann. Chem. (Liebig), **66**, 287. The latter says he obtained the salt from one part ammonium and two parts zinc chloride.

2. $ZnCl_2.NH_4Cl.2H_2O$. Hautz, *loc. cit.* He mixed one part of each constituent and obtained this salt in large shining leaves, he says.

3. $ZnCl_2.2NH_4Cl$. Rammelsberg. Ann. der phys. (Pogg.), **94**, 507 ; also Marignac, Ann. des Mines [5], **12**, 1.

4. $ZnCl_2.3NH_4Cl$. Marignac, *loc. cit.*

5. $ZnCl_2.NH_4Cl.$ }
6. $ZnCl_2.4NH_4Cl.$ } Dehérain, Bl. (1861), 51, says that

$ZnCl_2.NH_3$, $ZnCl_2.2NH_4$, and $ZnCl_2.NH_3$, when dissolved in hydrochloric acid, yield corresponding double chlorides.

7. $ZnCl_2.6NH_4Cl.\frac{2}{3}H_2O.$ } Berthelot and André, Ann. chim.
8. $ZnCl_2.3NH_4Cl.H_2O.$ }

phys. (6), **11**, 294–310. These chemists mention the existence of these two salts but do not state how they were obtained.

By working under various conditions, I was able to obtain only two double salts; *viz.*, Nos. 3 and 4 in the list above, which were also obtained by Marignac. He did not make a thorough study, but made a mixture in only one molecular proportion. As these salts were completely described by Marignac, I cannot do better than to give his own words. He says, " In his treatise on crystallographical chemistry, Rammelsberg describes the crystal forms of this salt, (*i. e.*, No. 3) to which he attributes the formula $ZnCl_2.2NH_4Cl$. An earlier analysis by Schindler made it appear to contain an equivalent of water. And it is to be noticed that the crystals described by Rammelsberg may be regarded as isomorphous with the stannous ammonium chloride described by the same chemist, of which he represents the composition by the formula $SnCl_2.2NH_4Cl.H_2O$. These considerations have induced me to undertake again the examination of these salts. The results have not answered to what I supposed, but they are not the less curious. They prove, in effect, the existence of two double salts, both anhydrous, and represented by the formulas (see 3 and 4 above). What is most singular is that these two salts, perfectly distinct as regards their appearance and their faces, have forms which can be derived from one another. However, one cannot call them isomorphous, since they do not mix in anywise in crystallizing, and there is no passage from the one to the other, although they are formed sometimes simultaneously in the same beaker.''

Marignac calls $ZnCl_2.2NH_4Cl$ the laminated salt and $ZnCl_2.3NH_4Cl$ the prismatic salt. He dried the salts in all cases at 100°, at which temperature they preserved their transparency and lost only a trace of hygroscopic water. The prismatic crystals are right rhombohedral prisms.

Diammonium Chlorozincate, $ZnCl_2.2NH_4Cl$.—Mixtures of zinc chloride and ammonium chloride were made in the molecular proportions of $3 : 1$, $2 : 1$, $1 : 1$, $1 : 2$. The same salt was obtained from all of them, the laminated salt of Marignac. It forms large shining plates. Sometimes a $1 : 2$ mixture gave the $1 : 3$ salt at first, and the $1 : 2$ salt in later crops. The mixtures were neutral or slightly acid.

0.2125 gram salt gave 0.0711 gram ZnO and 0.5036 gram AgCl.

0.1891 gram salt gave 0.0632 gram ZnO.

0.2456 gram salt gave 0.5776 gram AgCl.

	Calculated for $ZnCl_2.2NH_4Cl$.	I.	Found. II.	III.
Zn	26.83	26.86	26.84	....
Cl	58.32	58.60	....	58.16

Triammonium Chlorozincate, $ZnCl_2.3NH_4Cl$.—Solutions of zinc chloride and ammonium chloride, in the proportions of $1 : 3$, $1 : 4$, $1 : 6$, gave only the $1 : 3$ salt. In the $1 : 6$ solution, ammonium chloride crystallized out first.

0.1546 gram salt gave 0.0424 gram ZnO and 0.3759 gram AgCl.

0.4685 gram salt gave 0.1272 gram ZnO and 1.1267 grams AgCl.

	Calculated for $ZnCl_2.3NH_4Cl$.	I.	Found. II.
Zn	22.00	22.02	21.80
Cl	59.76	60.13	59.47

Solutions of zinc chloride and ammonium chloride were made in the proportions of $1 : 1$ and $1 : 4$, in concentrated hydrochloric acid in order to see if the strong acid would cause the formation of salts different from those just described. The first crop of crystals from the $1 : 1$ solution was the $1 : 3$ salt of Marignac, as was shown by their appearance and analysis. The other crops were composed of plates which proved to be the $1 : 2$ salt. The $1 : 4$ solution gave the $1 : 3$ salt.

Dehérain says that when $ZnCl_2.NH_3$ and $ZnCl_2.4NH_3$ are dissolved in hydrochloric acid, corresponding double salts are formed. According to Kane,[1] $ZnCl_2.4NH_3.H_2O$ is formed

[1] Ann. Chem. (Liebig), [2], **72**, 290.

when concentrated ammonia is added to a hot concentrated solution of zinc chloride, until the precipitate first formed is redissolved. On cooling, the salt is said to separate out in small brilliant plates with pearly luster. According to Marignac,[1] $ZnCl_2.2NH_3$ is often formed at once when the two solutions are brought together, as described by Kane. Kane says that, on further evaporation of the solution after removing the first crop of crystals, $ZnCl_2.2NH_3.\frac{1}{2}H_2O$ crystallizes out in radiating groups of square prisms of a brilliant vitreous luster. $ZnCl_2.NH_3$ is obtained, according to Kane, by heating $ZnCl_2.4NH_3.H_2O$ or $ZnCl_2.2NH_3.\frac{1}{2}H_2O$, ammonia and water being given off and a gummy mass remaining.

Following Kane's directions, as Dehérain also did, a compound was obtained, the analysis of which gave results agreeing fairly well with the formula $ZnCl_2.4NH_3.H_2O$. The determination of zinc gave a figure which was less than the theoretical per cent. by 1.6 per cent. Some of the compound was dissolved in hydrochloric acid and allowed to crystallize. Small prismatic crystals were obtained that resembled, in all respects, the 1 : 3 salt described by Marignac. A determination of zinc was made, 0.2397 gram giving 0.0647 gram ZnO, *i. e.*, 21.74 per cent., the theoretical being 22.00 per cent. for the 1 : 3 salt.

On heating the rest of the compound, $ZnCl_2.4NH_3.H_2O$, ammonia was given off and a gummy mass was left, as described by Kane. This was dissolved in hydrochloric acid and allowed to crystallize. Thin, shining plates were formed looking exactly like the 1 : 2 salt already described. It seems then, that dissolving these compounds in hydrochloric acid is equivalent to making solutions of zinc chloride and ammonium chloride in the proportions of 1 : 4 and 1 : 1, and we have seen that the former solution yields a 1 : 3 salt, while the latter yields a 1 : 2 salt.

[1] Ann. des Mines [5], **12**, 1.

SULPHONATION OF THE PARAFFINS.
By R. A. Worstall.

The comparative ease with which the paraffins can be nitrated, as set forth in a previous communication,[1] suggested the idea that under proper conditions they might also be capable of direct sulphonation. So far as I am aware, there is no recorded instance of such sulphonation having been accomplished. It is stated by all authorities, and is probably accepted without question, that neither sulphuric acid nor its anhydride will react with aliphatic hydrocarbons.

A few preliminary experiments with octane and sulphuric acid demonstrated to my own satisfaction that a reaction certainly took place between the two. But for some time all such experiments led to no definite results, simply because it was assumed that the reaction would take place, if at all, only with great difficulty, and the method of sulphonation at first employed was far too vigorous. It was not until it was recognized that this reaction, like the nitration, is in reality easily brought about, that any progress was made.

In the preliminary experiments, for which octane was employed, the sulphonation was attempted by boiling the hydrocarbon with fuming sulphuric acid. While it was evident, from the blackening of the acid and the evolution of sulphur dioxide, that a reaction was taking place, nothing but a tarry mass was left in the flask, and from it no sulphonic acids could be obtained. It was subsequently found that it is necessary to heat the two only to the boiling-point of the hydrocarbon, or even lower, and that in fact any considerable increase in temperature above this point destroys the sulphonic acids.

Comparative experiments were tried with octane, using sulphuric acid of specific gravity 1.84, and the fuming acid, both in sealed tubes and open flasks. While in either case both acids react to form sulphonic acids, the best results and the largest yield were obtained by using successive small portions of fuming sulphuric acid in an open flask with return-con-

[1] This Journal, **20**, 202.

denser, keeping the contents near the boiling-point of the hydrocarbon, and shaking vigorously. By this method, apparently only the monosulphonic acids were formed, whereas, as will be seen later, the action of sulphuric anhydride alone gives rise to the formation of disulphonic acids.

The hydrocarbons which have been employed are the normal paraffins, hexane, heptane, and octane.[1] Each hydrocarbon was the residue left after reducing 200 or 300 grams of the original hydrocarbon by nitration to 40 or 50 grams. This residue in each case was distilled, boiled with sodium for a day to free it from nitro-compounds, redistilled, the distillate washed with cold fuming sulphuric acid, and with caustic soda, dried, and again distilled. The boiling-points were sharp and constant, and the treatment which each had undergone would seem to exclude any possibility of the presence of hydrocarbons other than the paraffins.

Hexane, C_6H_{14}.

The normal hexane employed boiled at 68°–69° (uncorr.), and its specific gravity was 0.6860 at $\frac{20}{4}°$. For the production of the monosulphonic acid the hydrocarbon was heated on the steam-bath with successive small portions of fuming sulphuric acid in a flask with return-condenser. The flask was shaken vigorously throughout the reaction, the acid layer becoming deep brown, and considerable sulphur dioxide being evolved. By repeating the treatment with the residual hydrocarbon, a yield of from 30 to 40 per cent. of the theoretical was obtained, the rest of the hydrocarbon being oxidized to carbon dioxide and water.

The mixed acids were diluted with water and the brown solution thus obtained neutralized with barium carbonate. The filtrate was boiled to decompose any acid carbonate of barium, filtered again, and the filtrate evaporated to dryness. The salts of the sulphonic acids examined were so extremely soluble in water that no well-defined crystals could be obtained from aqueous solution, and no better results were obtained from dilute alcoholic solutions. And on account of lack of time the salts have been purified, as well as possible, by other means and the anhydrous salt employed.

[1] For the original hydrocarbons I am indebted to Dr. C. F. Mabery.

Barium Hexylsulphonate, $(C_6H_{13}SO_3)_2Ba$. — The barium compound as obtained consisted of brown plates. By boiling with animal charcoal, filtering, and evaporating to dryness, the brown color is removed, leaving the salt light-yellow. Analysis gave the following results:

0.0736 gram gave 0.0368 gram $BaSO_4$ (for barium).
0.1025 gram gave 0.1035 gram $BaSO_4$ (for sulphur).

	Calculated for $(C_6H_{13}SO_3)_2Ba$.	Found.
Ba	29.33	29.48
S	13.71	13.85

Barium was determined by igniting with sulphuric acid to barium sulphate. Sulphur by fusion with sodium carbonate and potassium nitrate and the estimation of sulphuric acid in the water solution of the fusion.

Barium hexylsulphonate is a neutral salt, light-yellow in color, extremely soluble in water, insoluble in alcohol, ether, and other organic solvents. It is precipitated from its aqueous solution in an amorphous form by alcohol.

Lead Hexylsulphonate, $(C_6H_{13}SO_3)_2Pb$.—The barium salt was converted into that of lead by dissolving in water, precipitating the barium with a slight excess of sulphuric acid, neutralizing the filtrate with lead carbonate, filtering, and evaporating to dryness. Analysis of the salt gave the following results:

0.0844 gram gave 0.0477 gram $PbSO_4$.
0.1393 gram gave 0.1211 gram $BaSO_4$.

	Calculated for $(C_6H_{13}SO_3)_2Pb$.	Found.
Pb	38.55	38.61
S	11.92	11.91

The lead salt resembles the barium salt in all its properties.

Hexylsulphonic Acid, $C_6H_{13}SO_3H$.—The lead salt was dissolved in water and the lead removed by hydrogen sulphide. The filtered solution was then evaporated to dryness, again dissolved in water, and filtered to remove traces of lead sulphide, and again evaporated to dryness. The acid was then dried at 105° for an hour.

0.0706 gram acid gave 0.1006 gram $BaSO_4$.

	Calculated for $C_6H_{13}SO_3H$.	Found.
S	19.27	19.54

Hexylsulphonic acid is a thick liquid, light-brown in color. It is readily soluble in alcohol and water, insoluble in ether, chloroform, etc.; soluble in hot benzol, and is at once extracted by water from the latter solution. It could not be crystallized. It has an intense acid taste and strong acid reaction, all of its salts appearing to be soluble in water. The amount obtained was so small that nothing further could be done in the way of identification.

Action of Sulphuric Anhydride.

To determine the action of sulphuric anhydride upon hexane, the hydrocarbon was placed in a flask fitted with a two-hole rubber stopper, through which passed a reflux-condenser and a gas-delivery tube leading just above the surface of the hydrocarbon.

This oil was set to boiling upon the steam-bath, and a stream of sulphur trioxide, made by distilling fuming sulphuric acid, was passed in through the delivery-tube. A reaction took place at once with the production of heavy brown vapors which condensed to a liquid upon the walls of the flask, while from the evolution of sulphurous acid it was evident that oxidation was also resulting.

After passing in the anhydride for a short time, the flask was cooled, and the unchanged hydrocarbon poured out. The sulphonic acid was washed out with water, and the process repeated with the residual hydrocarbon, the best results being obtained in this way. Thirty grams of hexane were treated with the anhydride for ten minutes. The loss in weight of the hydrocarbon was 6 grams, and from this 6 grams of barium salt was obtained. The residue of 25 grams hexane was again treated in the same way for twenty-five minutes, when it lost 13 grams and yielded 11 grams of the barium salt. By continuing the sulphonation in this way, the yield of disulphonic acid was about 40 per cent. of the theoretical, the rest of the hydrocarbon being completely oxidized.

Barium Hexyldisulphonate, $C_6H_{12}(SO_3)_2Ba$.—The solution of the sulphonic acid as above obtained, was converted into the barium salt by means of barium carbonate. This salt was purified with bone-black, and dried for an hour at 105°.

0.1014 gram gave 0.0615 gram $BaSO_4$ (for barium).

0.1370 gram gave 0.1625 gram $BaSO_4$ (for sulphur).

	Calculated for $C_6H_{12}(SO_3)_2Ba$.	Found.
Ba	35.95	35.71
S	16.80	16.36

In its solubilities and general properties this compound closely resembles the barium salt of the monosulphonic acid. It is golden-yellow, soluble in water, and quite deliquescent, absorbing moisture rapidly from the air.

Lead Hexyldisulphonate, $C_6H_{12}(SO_3)_2Pb$.—The barium salt was converted into the lead salt in the usual way. The latter, after drying for an hour at 105°, gave the following results upon analysis :

0.1326 gram gave 0.0882 gram $PbSO_4$.

0.1244 gram gave 0.1296 gram $BaSO_4$.

By combustion with lead chromate, 0.1512 gram gave 0.0870 gram CO_2; and 0.0347 gram H_2O.

	Calculated for $C_6H_{12}(SO_3)_2Pb$.	Found.
C	15.96	15.69
H	2.66	2.56
S	14.19	14.27
Pb	45.89	45.45

Golden-yellow salt, with a slight acid reaction ; extremely soluble in water, rapidly absorbing moisture from the air ; insoluble in alcohol, ether, etc.

Hexyldisulphonic Acid, $C_6H_{12}(SO_3H)_2$.—The free acid was obtained from the lead salt by removing the lead with hydrogen sulphide. The filtrate was evaporated to dryness, the residue extracted with hot alcohol, filtered, and the alcoholic extract evaporated to dryness. Analysis gave the following results :

0.0470 gram gave 0.0895 gram $BaSO_4$.

By combustion with lead chromate, 0.1356 gram gave 0.1449 gram CO_2; and 0.0645 gram H_2O.

	Calculated for $C_6H_{12}(SO_3H)_2$.	Found.
C	29.27	29.14
H	5.69	5.29
S	26.01	26.17

Hexyldisulphonic acid is a thick sirup that gave no signs of crystallizing ; brown in color ; extremely soluble in water, absorbing moisture rapidly from the air ; soluble in hot benzol and alcohol ; insoluble in petroleum, ether, etc. ; strong acid reaction and sharp taste. All its salts appear to be soluble in water.

Heptane, C_7H_{16}.

The heptane employed was the normal hydrocarbon boiling at 98°–99°, specific gravity 0.6980, at $\frac{20°}{20°}$. For the formation of the monosulphonic acid the hydrocarbon was heated on the steam-bath with successive small portions of fuming sulphuric acid in a flask with return-condenser. The flask was well shaken during the reaction, the acid layer becoming deep brown. Thirty grams of heptane by warming with four successive portions of fuming acid lost 15 grams and yielded 12 grams of the barium sulphonate. By continuing the sulphonation with the residue, the yield amounted to about the same as for hexane—that is, about 40 per cent. of the theoretical. The mixed acids were diluted with water, giving a green solution which, when neutralized with barium carbonate, became light-brown.

Barium Heptylsulphonate, $(C_7H_{15}SO_3)_2Ba$. — The barium salt was purified by boiling with bone-black, filtering, and evaporating to dryness. Analysis gave the following results :

0.2070 gram gave 0.0961 gram $BaSO_4$ (for barium).
0.0923 gram gave 0.0877 gram $BaSO_4$ (for sulphur).

	Calculated for $(C_7H_{15}SO_3)_2Ba$.	Found.
Ba	27.68	27.35
S	12.93	13.01

Barium heptylsulphonate resembles the corresponding derivative of hexane in its properties.

Lead Heptylsulphonate, $(C_7H_{15}SO_3)_2Pb$. — The barium salt was converted into that of lead in the usual manner and the latter analyzed.

0.1562 gram gave 0.0831 gram $PbSO_4$.

0.1113 gram gave 0.0923 gram $BaSO_4$.

	Calculated for $(C_7H_{15}SO_3)_2Pb$.	Found.
Pb	36.64	36.40
S	11.33	11.38

It is a light-yellow salt, very soluble in water, insoluble in alcohol, etc.; resembling the barium compound closely.

Heptylsulphonic Acid, $C_7H_{15}SO_3H$.—The free acid was obtained from the lead salt by means of hydrogen sulphide. After purifying and drying at 105°, a sulphur determination was made.

0.3191 gram gave 0.4178 gram $BaSO_4$.

	Calculated for $C_7H_{15}SO_3H$.	Found.
S	17.77	17.96

The free sulphonic acid is a thick brown sirup, that could not be crystallized; soluble in alcohol; extremely soluble in water; insoluble in ether, etc. Upon warming with phosphorus pentachloride a reaction took place readily with the evolution of hydrochloric acid. From the product of the reaction an oily liquid was obtained, insoluble in water, apparently a sulphonchloride. This was dissolved in alcohol and the solution saturated with dry ammonia gas. In this way a sulphonamide was apparently produced. Determination of sulphur and nitrogen showed it to be an impure heptylsulphonamide, but not a sufficient amount was obtained for further examination.

Action of Sulphuric Anhydride.

When heptane was set to boiling gently upon a steambath, and sulphur trioxide passed in, in the manner already described for hexane, a vigorous reaction took place. Heavy brown vapors were formed, condensing to a liquid on the walls of the flask, consisting of the disulphonic acid. At the same time considerable sulphur dioxide was evolved, in consequence of the oxidation of part of the hydrocarbon.

Barium Heptyldisulphonate, $C_7H_{14}(SO_3)_2Ba$.—The sulphonic acid was isolated by diluting with water and neutralizing with barium carbonate. The barium salt thus obtained, after

purifying with bone-black and drying at 105°, was analyzed.

0.1776 gram gave 0.1040 gram $BaSO_4$ (for barium).

0.1330 gram gave 0.1525 gran $BaSO_4$ (for sulphur).

	Calculated for $C_7H_{14}(SO_3)_2Ba$.	Found.
Ba	34.68	34.44
S	16.20	15.81

It is a light-yellow salt of neutral reaction, resembling in its solubilities and other properties the corresponding derivative of hexane.

Lead Heptyldisulphonate, $C_7H_{14}(SO_3)_2Pb$.—The barium salt was converted into that of lead in the usual manner and the latter analyzed.

0.1395 gram gave 0.0901 gram $PbSO_4$.

0.1034 gram gave 0.1029 gram $BaSO_4$.

By combustion with lead chromate, 0.2646 gram gave 0.1743 gram CO_2, and 0.0678 gram H_2O.

	Calculated for $C_7H_{14}(SO_3)_2Pb$.	Found.
C	18.06	17.96
H	3.01	2.85
S	13.76	13.63
Pb	44.51	44.20

It is a light-yellow salt, quite deliquescent; extremely soluble in water; insoluble in alcohol, ether, etc.; slight acid reaction in aqueous solution.

Heptyldisulphonic Acid, $C_7H_{14}(SO_3H)_2$.—The free acid was obtained from the lead salt by removing the lead with hydrogen sulphide. The aqueous solution of the acid was evaporated to dryness, extracted with alcohol, filtered, and again evaporated to dryness. After drying for an hour at 105° the acid was analyzed.

0.0913 gram gave 0.1608 gram $BaSO_4$.

By combustion with lead chromate, 0.1486 gram gave 0.1738 gram CO_2, and 0.0808 gram H_2O.

	Calculated for $C_7H_{14}(SO_3H)_2$.	Found.
C	32.30	31.90
H	6.15	6.05
S	24.61	24.21

Heptyldisulphonic acid is a pasty, dark-brown mass. It could not be solidified or crystallized by standing. It is extremely soluble in water, rapidly absorbing sufficient moisture from the air to become liquid; soluble in hot alcohol and benzol; insoluble in ether, petroleum ether, etc.; strong acid reaction and intense acid taste. All its salts are soluble in water.

Octane, C_8H_{18}.

The normal octane employed boiled at 124°–125° (uncorr.), and its specific gravity was 0.7123 at $\frac{20}{4}°$.

The monosulphonic acid was prepared by heating the hydrocarbon with about five times its weight of fuming sulphuric acid in a flask with return-condenser. The flask was vigorously shaken and the temperature was not allowed to exceed 125°. The acid layer became deep-brown and considerable sulphur dioxide was evolved. In one case, 15 grams octane, when treated in this manner three times with fresh portions of the fuming acid, lost 7 grams, and yielded 6 grams of the barium sulphonate. By repeating the sulphonation with the residual hydrocarbon a yield of from 30 to 40 per cent. of the theoretical was obtained.

Barium Octylsulphonate, $(C_8H_{17}SO_3)_2Ba$.—The mixed acids were diluted with water and neutralized with barium carbonate. The barium salt thus obtained was purified with boneblack, dried at 105°, and analyzed.

0.2808 gram gave 0.1254 gram $BaSO_4$ (for barium).
0.2128 gram gave 0.1925 gram $BaSO_4$ (for sulphur).

	Calculated for $(C_8H_{17}SO_3)_2Ba$.	Found.
Ba	26.19	26.25
S	12.26	12.44

It is a light-yellow salt, resembling in solubilities and general properties the corresponding derivatives of heptane and hexane.

Lead Octylsulphonate, $(C_8H_{17}SO_3)_2Pb$.—The barium salt was converted into the lead salt and the latter, after drying at 105°, was analyzed.

0.1652 gram gave 0.0850 gram $PbSO_4$.
0.1628 gram gave 0.1310 gram $BaSO_4$.

	Calculated for $(C_8H_{17}SO_3)_2Pb.$	Found.
Pb	34.91	35.05
S	10.79	10.93

The lead salt resembled the barium salt in appearance and properties.

Octylsulphonic Acid, $C_8H_{17}SO_3H$.—The free acid was obtained from the lead salt by removing the lead with hydrogen sulphide. The acid was dried at 105°.

0.1041 gram gave 0.1277 gram $BaSO_4$.

	Calculated for $C_8H_{17}SO_3H.$	Found.
S	16.49	16.71

Octylsulphonic acid is a thick sirup, very soluble in water, soluble in alcohol, insoluble in petroleum ether, carbon disulphide, etc. It has a strong acid reaction. All its salts are soluble in water.

Action of Sulphuric Anhydride.

When sulphur trioxide is passed into gently boiling octane in the manner described for hexane, a similar reaction occurs with the formation of a disulphonic acid. Considerable oxidation results at the same time, and sulphur dioxide is formed.

Octyldisulphonic Acid, $C_8H_{16}(SO_3H)_2$.—The brown liquid produced by the action of the anhydride was diluted with water, neutralized with lead carbonate, and the free acid obtained from the lead salt by means of hydrogen sulphide. The acid solution was evaporated to dryness, extracted with hot alcohol, and the alcoholic solution evaporated to dryness. Analysis of the acid gave the following results :

By combustion with lead chromate, 0.1128 gram gave 0.1416 gram CO_2, and 0.0664 gram H_2O.

	Calculated for $C_8H_{16}(SO_3H)_2.$	Found.
C	34.66	34.24
H	6.49	6.38

Octyldisulphonic acid is a brown, pasty mass, very deliquescent, extremely soluble in water, slowly soluble in alcohol and hot benzol; insoluble in ether, etc.; strong acid reaction. All its salts are soluble in water.

When sulphuric anhydride was passed into the boiling hydrocarbons in the manner described, there was formed in each case, in addition to the sulphonic acids, a dark-brown solid, insoluble in water. When the solution was diluted with water, the latter compound was filtered off, washed with hot water, and dried. In the case of hexane and heptane this product amounted to only a very small fraction of a per cent., the total amount obtained from each being about a tenth of a gram. From octane, however, the amount obtained amounted to several per cent. These compounds were, after drying, brittle, lustrous solids of a dark-brown color, insoluble in water and all organic solvents ; readily oxidized by heating with strong nitric acid. They were at first thought to be sulphones, but analysis showed that this was not the case. The analytical results obtained were as follows :

	1. (From C_6H_{14}).	2. (From C_7H_{16}).	3. (from C_8H_{18}).
C	47.16	49.51	51.90
H	3.78	4.08	4.50
S	....	....	11.44

These results would seem to show that the products were definite compounds of a regular series, high in oxygen (possibly oxysulphones). But from the very small quantities obtained and their indifference to all reagents, their identity could not be established.

From the results of the investigation, the following conclusions may be drawn :

1. Aliphatic hydrocarbons, as well as the aromatic, are readily capable of direct sulphonation.

2. Regulation of temperature is essential to the proper control of the reaction. Cold fuming sulphuric acid is without perceptible action upon the pure hydrocarbon. But if the temperature employed be too high, the sulphonic acids, which are at first formed, are destroyed. The correct temperature to employ would seem to be the boiling-point of the hydrocarbon.

3. Gentle methods of sulphonation, such as warming with fuming sulphuric acid, seem to yield only the monosulphonic acid, while more vigorous methods, as the use of sulphuric an-

hydride, result in the formation of disulphonic acids. It appeared occasionally, from the difficulty experienced in purifying the salts of the monosulphonic acid, that some disulphonic acid had been formed at the same time, even by the former method.

4. By the methods described yields of about 40 per cent. of the theoretical can be obtained, both of the mono- and of the disulphonic acids. The rest of the hydrocarbon is oxidized to carbon dioxide and water.

The preliminary results communicated in a former paper[1] in regard to the nitration of paraffins are being confirmed by a more complete and extended investigation of this reaction now in progress. Yields of mixed nitroparaffins have been obtained, amounting in the case of nonane to 70 per cent. of the theoretical, of octane to 55 per cent., and of heptane to 40 per cent. These results, in connection with those obtained by the sulphonation, certainly disprove the statements constantly met with, even in the latest text-books of organic chemistry, that aliphatic hydrocarbons differ from the aromatic hydrocarbons, in that the former are not capable of nitration by nitric acid, or of sulphonation by sulphuric acid.

Orndorff and Young[2] state that they found propane to be slowly absorbed by fuming sulphuric acid, the acid turning first red, then brown, and express surprise that propane, a member of the marsh gas series, should thus be absorbed. This statement, taken in connection with the peculiar fact that the three paraffins examined can be sulphonated *at their boiling-points*, suggests that the example cited by Orndorff and Young was one of actual sulphonation. This investigation is therefore being extended to the behavior of the gaseous members of the aliphatic series towards fuming sulphuric acid.

LAFAYETTE, IND., May, 1898.

[1] *Loc. cit.*   [2] This JOURNAL, **15**, 261.

THE FORMATION OF HYDRAZIDES BY THE ACTION OF PHENYLHYDRAZINE UPON ORGANIC ACIDS IN THE COLD.

By Virgil L. Leighton.

The phenylhydrazides of organic acids have been made by the following methods : Heating the acid or a solution of the acid with phenylhydrazine ;[1] action of the base upon the chloride of the acid ;[2] action of the sodium derivative of phenylhydrazine upon the chloride of the acid ;[3] action of the base upon the amide of the acid ;[4] treating the ester with phenylhydrazine ;[5] and by the action of phenylhydrazine upon the acetylanhydride of the acid.[6]

It came under my observation that phenylhydrazine acetate on standing a few days at the ordinary temperature in a solution of acetic acid passed over into the hydrazide. As no observation of this kind appears to have been made before, other acids were tried, to determine if the reaction is general.

The course of procedure was, in the case of all liquid acids, first to make the salt by treating the acid with the calculated amount of phenylhydrazine, care being taken in all cases to avoid heating. The salt thus formed was dissolved in as little of the acid as possible, and the mixture allowed to stand at the ordinary temperature until the reaction seemed complete. A little water was then added (usually about four times the weight of the acid used), and the crystals filtered off. In this way the phenylhydrazides of formic, acetic, propionic, isobutyric, isocaproic, and heptoic acids have been made. This method will undoubtedly be of considerable advantage for obtaining the hydrazides of acids which cannot be heated.

[1] Fischer : Ann. Chem. (Liebig), **190**, 29 ; and Ber. d. chem. Ges., **22**, 2728 ; Bülow: Ann. Chem. (Liebig, **236**), 134.

[2] Fischer : Ann. Chem. (Liebig), **190**, 125 ; Freund and Goldsmith : Ber. d. chem. Ges., 21, 2456 ; Gattermann : *Ibid*, **25**, 1081.

[3] Michaelis and Schmidt : Ann. Chem. (Liebig), **252**, 301.

[4] Just : Ber. d. chem. Ges., **19**, 1201 ; Freund and Goldsmith : *Ibid*, **21**, 2461.

[5] Fischer : Ann. Chem. (Liebig), **190**, 131 ; Freund and Goldsmith : Ber. d. chem. Ges., **21**, 1241.

[6] Autenrieth : Ber. d. chem. Ges., **20**, 3187.

Experiments.

Formylphenylhydrazide.[1]—Two grams of phenylhydrazine were dissolved in 2.4 grams of formic acid, care being taken to avoid heating. Crystals of formylphenylhydrazide began to appear after about one-half hour; after two hours the mass was nearly solid. It was allowed to stand twenty-four hours, then a little water was added; the crystals were separated and washed with water, whereby 1.8 grams were obtained (71.7 per cent. of the theory). Crystallized from alcohol, and dried in a vacuum over sulphuric acid, it melted at 144°–145° and gave, on analysis, the following results:

0.1746 gram of substance gave 0.3979 gram of carbon dioxide and 0.0982 gram of water.

	Calculated for $C_6H_5N_2H_2CHO$.	Found.
C	61.77	61.91
H	5.88	6.26

Acetylphenylhyrazide.[2]—Two grams of phenylhydrazine were dissolved in 3.4 grams of acetic acid. Crystals began to appear after two days. It was allowed to stand two days longer, and water was then added; the crystals were separated by filtration, and washed with water. 1.7 grams were obtained (61.1 per cent. of the theory), which crystallized from dilute alcohol melted at 128° and agreed in properties with acetylphenylhydrazide. An attempt to form this compound by dissolving phenylhydrazine acetate in water and allowing the solution to stand at the ordinary temperature gave negative results.

Propionylphenylhydrazide.[2]—Two grams of phenylhydrazine were dissolved in 4 grams of propionic acid. On standing over night some crystals of propionylphenylhydrazide were formed. After five days, water was added, and the crystals were separated and washed with water. 2.6 grams were obtained (86.6 per cent. of the theory). Crystallized from alcohol it melted at 157°–158° (Freund and Goldsmith gave the melting-point as 157°–158°).

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[1] This compound was first made by Just: Ber. d. chem. Ges., **19**, 1201.

[2] First obtained by Fischer: Ann. Chem. (Liebig), **190**, 129.

[3] First made by Freund and Goldsmith: Ber. d. chem. Ges., **21**, 2461.

Isobutyrylphenylhydrazide.—To 1.4 grams of phenylhydrazine were added 4.5 grams of isobutyric acid. The mass began to crystallize after five days. Some hydrazide was formed before that time, as was shown by adding water to a small portion that had stood but three days, crystals separating at once. After standing seven days water was added, and 0.6 gram obtained (25 per cent. of the theory).

Isobutyrylphenylhydrazide is nearly insoluble in cold water, moderately soluble in cold, easily in hot alcohol. Crystallized from the latter it appears as slightly pink, rectangular tablets (sometimes hexagonal), melting at 142°–143°. The analysis gave the following results :

0.1211 gram of substance gave 0.2982 gram of carbon dioxide and 0.0884 gram of water.

	Calculated for $C_6H_5N_2H_2COC_3H_7$.	Found.
C	67.41	67.15
H	7.86	8.09

Isohexylphenylhydrazide.—0.4 gram of phenylhydrazine was dissolved in 2 grams of isocaproic (isobutylacetic) acid. Some hydrazide was deposited after twenty-four hours. It was allowed to stand five days, water was then added and 0.35 gram obtained (47.1 per cent. of the theory). It is nearly insoluble in cold water, soluble in alcohol, nearly insoluble in cold, easily in hot ligroïn, from which it crystallizes in thin transparent crystals, melting at 144°–145°. The analysis gave the following results :

0.1904 gram of substance gave 0.4887 gram of carbon dioxide and 0.1558 gram of water.

	Calculated for $C_6H_5N_2H_2COC_5H_{11}$.	Found.
C	70.24	69.99
H	8.78	9.10

Heptylphenylhydrazide.—0.4 gram of phenylhydrazine was dissolved in 1 gram of heptoic acid. After forty hours a considerable quantity of the hydrazide had crystallized out. After six days water was added and 0.69 gram obtained (86.4 per cent. of the theory). The product is nearly insoluble in cold water, difficultly soluble in cold, easily in hot alcohol,

from which it crystallizes in thin transparent prisms melting at 103°–104°.

0.1440 gram of substance gave 0.3754 gram of carbon dioxide and 0.1178 gram of water.

	Calculated for $C_6H_5N_2H_2COC_6H_{13}$.	Found.
C	70.91	71.08
H	9.09	9.16

Action of Phenylhydrazine upon Acetylenedicarboxylic Acid.

As has been shown[1] phenylhydrazine hydrochloride acts upon acetylenedicarboxylic acid in aqueous solution to form 1-phenyl-5-pyrazolon-3-carboxylic acid. The following experiments show that in the presence of acetic acid, or if an excess of the acid itself is used, the same compound is formed; but if an excess of phenylhydrazine is used, a different compound results.

To 0.5 gram of acetylenedicarboxylic acid, dissolved in 2 grams of glacial acetic acid, was added 0.5 gram of phenylhydrazine in 3 grams of glacial acetic acid. After standing three days 0.87 gram of crystallized substance was obtained which, washed with water and crystallized from alcohol, began to turn brown at 240° and decomposed at 265°–266°, (characteristic of 1-phenyl-5-pyrazolon-3-carboxylic acid).[2] With a solution of ferric chloride it gave a deep violet color.

To 0.2 gram of acetylenedicarboxylic acid, dissolved in 4 cc. of water, 0.2 gram of phenylhydrazine was added. Crystals began to separate after about two hours. After twenty-four hours 0.28 gram was obtained, which, crystallized from alcohol, decomposed at 265°–266°.

An experiment made in aqueous solution with an excess of phenylhydrazine gave a crystalline product possessing none of the properties of 1-phenyl-5-pyrazalon-3-carboxylic acid. Its composition has not yet been determined.

TUFTS COLLEGE, May, 1898.

[1] Michael and Bucher, communicated by the authors.
[2] Michael and Bucher.

ALIPHATIC SULPHONIC ACIDS.

II. ETHYLENESULPHONIC ACIDS.

By Elmer P. Kohler.

In a previous paper[1] I showed that unsaturated sulphonic acids can be prepared by decomposing the chlorides of saturated polysulphonic acids with water. The method was illustrated with (1,2)-ethanedisulphone chloride, which reacts with boiling water to form ethylenesulphonic acid:

$$\begin{array}{c} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{array} + H_2O = \begin{array}{c} CH_2 \\ || \\ CHSO_3H \end{array} + SO_2 + 2HCl.$$
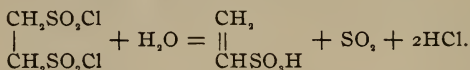
That the product of this reaction is the lowest member of the unsaturated sulphonic acid series (I), and not an isomeric disulphonic acid (II),

$$\begin{array}{cc} CH_2 & CH_2SO_3H \\ || & | \\ CHSO_3H & CH \\ & || \\ & CH \\ & | \\ & CH_2SO_3H \\ \quad\text{I.} & \quad\text{II.} \end{array}$$
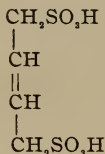
was shown by the fact that the salts of the acid combine with acid sulphites to form the corresponding salts of (1,2)-ethanedisulphonic acid:

$$\begin{array}{c} CH_2 \\ || \\ CHSO_3Na \end{array} + \begin{array}{c} SO_3Na \\ | \\ H \end{array} = \begin{array}{c} CH_2SO_3Na \\ | \\ CH_2SO_3Na \end{array}.$$
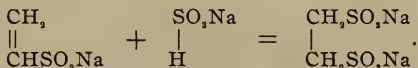
In confirmation of this view, it has since been found that the acid can be reduced to ethanesulphonic acid, and that it combines with water and the halogen acids to form derivatives of ethanesulphonic acid.

Methods of Preparation.

1. *From (1,2)-Ethanedisulphone Chloride.*—A suitable quantity of (1,2).ethanedisulphone chloride is placed in a flask

[1] This Journal, **19**, 730.

with about five times its weight of water, the flask connected with an inverted condenser, and the whole boiled until all the chloride has disappeared. The resulting liquid is then transferred to an evaporating dish and concentrated on a steam-bath until a few drops of the residue no longer give a precipitate with silver nitrate solution. The amber-colored liquid still contains some (1,2)-ethanedisulphonic acid mixed with the ethylenesulphonic acid. If the liquid is allowed to stand for a few days most of the disulphonic acid separates out in the form of long colorless needles, which can be removed by filtration. A still further separation can be obtained by mixing the filtrate with its own volume of glacial acetic acid, and again allowing it to stand for a few days. To get pure ethylenesulphonic acid, however, it is necessary to make use of the salts. All the salts of (1,2)-ethanedisulphonic acid are insoluble in 95 per cent. alcohol, while the potassium, sodium, and ammonium salts of ethylenesulphonic acid are readily soluble in alcohol of this strength. To get the free acid it is best to use the ammonium salt. The amber-colored liquid is diluted to twice its volume, neutralized with solid ammonium carbonate, and evaporated to dryness. To remove the last traces of water, without decomposing the unsaturated sulphonic acid, it is necessary to add small quantities of absolute alcohol and repeat the evaporation. The fine, yellowish powder thus obtained is then transferred to a flask connected with an inverted condenser, and boiled with absolute alcohol. From the alcoholic solution the ammonium salt of the unsaturated acid crystallizes, on cooling, in perfectly pure condition.

To pass back to the acid, the ammonium salt is changed into the lead salt by boiling the aqueous solution with pure lead carbonate, the lead removed by precipitation as sulphide, and the resulting solution evaporated on the water-bath, and over sulphuric acid. The acid obtained in this way is an oily liquid without any tendency toward crystallization. It can stand over phosphorus pentoxide for months without change, and glacial acetic acid—the best solvent for aliphatic sulphonic acids—deposits it as an oil. The analyses show that it is pure ethylenesulphonic acid.

I. 0.3280 gram substance gave 0.2660 gram CO_2 and 0.1095 gram H_2O.

II. 0.4162 gram substance gave 0.3365 gram CO_2 and 0.1392 gram H_2O.

III. 0.2515 gram substance gave 0.5435 gram $BaSO_4$.

IV. 0.2050 gram substance gave 0.4430 gram $BaSO_4$.

	Calculated for $C_2H_4SO_3$.	I.	II.	III.	IV.
			Found.		
C	22.2	22.1	21.9	....	....
H	3.7	3.9	3.8	....	....
S	29.6	....	....	29.71	29.8

The acid mixes, in all proportions, with water, alcohol, and glacial acetic acid. It is difficultly soluble in ether and chloroform.

2. *From (1,2)-Bromethanesulphone Chloride.*—When (1,2)-bromethanesulphone chloride is distilled under atmospheric pressure it undergoes slight decomposition accompanied by evolution of hydrobromic acid. The distillate reacts with bromine, indicating the presence of an unsaturated compound. By distilling under increased pressure the amount of decomposition can be considerably increased. 50 grams of the sulphone chloride were slowly distilled under an increased pressure of about 1 meter of mercury, and the process repeated with the distillate until no further evolution of hydrobromic acid was observed. The resulting liquid was a mixture of sulphone chlorides which could not be separated by fractional distillation under any pressure. It was, therefore, decomposed by boiling with water, the hydrochloric acid precipitated as lead chloride, the lead removed as sulphide, and the acid neutralized with potassium carbonate. The mixture of salts obtained by evaporating this liquid to dryness was separated by recrystallization from alcohol and found to contain about equal amounts of (1,2)-bromethanesulphonate and ethylenesulphonate. From 50 grams of chloride 8.6 grams of potassium ethylenesulphonate were obtained. The solution obtained by neutralizing the mixed chlorides contained no hydrobromic acid, hence the unsaturated acid must have been formed during distillation.

$$
\begin{array}{l}
CH_2Br \\
| \\
CH_2SO_2Cl
\end{array}
=
\begin{array}{l}
CH_2 \\
\| \\
CHSO_2Cl
\end{array}
+ HBr.
$$
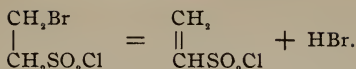
3. *From Isethionic Acid.*—As is well known, isethionates, when heated to 200°, lose water and pass almost quantitatively into di-isethionates:

$$
2
\begin{array}{l}
CH_2OH \\
| \\
CH_2SO_3K
\end{array}
= SO_3KCH_2CH_2-O-CH_2CH_2SO_3K + H_2O.
$$
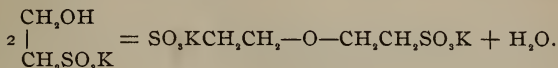
At a higher temperature the di-isethionates are decomposed, the sulphuric acid group being split off as sulphite. If, however, the isethionates are first changed into the acetic acid esters and then heated, acetic acid is split off, and the corresponding salts of ethylenesulphonic acid are formed. 40 grams of potassium isethionate were boiled with acetyl chloride until no further elimination of hydrochloric acid took place. The liquid was evaporated to dryness and the product crystallized from absolute alcohol. The salt, heated in a shallow vessel in an oil-bath began to soften at 160°. At 170° the odor of acetic acid became perceptible, while at 185° the salt began to froth, and soon solidified to a dark, glassy mass. This was dissolved in 95 per cent. alcohol, the solution decolorized with bone-black, and evaporated to crystallization. 18.8 grams of pure potassium ethylenesulphonate were obtained.

$$
\begin{array}{l}
CH_2O.COCH_3 \\
| \\
CH_2SO_3K
\end{array}
=
\begin{array}{l}
CH_2 \\
\| \\
CH_2SO_3K
\end{array}
+ CH_3CO_2H.
$$
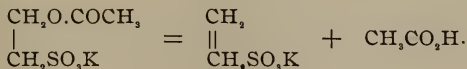
The method works equally well with sodium, potassium, and barium isethionates, but does not give good results with ammonium isethionate. The reaction promises to be particularly valuable for the preparation of more complex unsaturated sulphonic acids.

Salts of Ethylenesulphonic Acid.

The ammonium salt is readily obtained in perfectly pure condition, by neutralizing the acid with ammonium carbonate, evaporating to dryness, and crystallizing the residue from absolute alcohol.

I. 0.4165 gram salt gave 37.1 cc. N, at 27° and under a pressure of 748 mm.

II. 0.3212 gram salt gave 30.2 cc. N, at 28° and under a pressure of 744 mm.

	Calculated for $C_2H_7NSO_2$.	I.	Found. II.
N	11.2	11.2	11.4

The salt is extremely soluble in water, moderately soluble in cold aqueous, and boiling absolute alcohol; insoluble in ether. If its solution in aqueous alcohol is allowed to evaporate spontaneously, it separates in large orthorhombic tables. From a solution in boiling absolute alcohol it separates, on cooling, in short needles or prisms. Especially characteristic is its behavior on heating. If a small quantity is heated rapidly in a capillary tube, it melts completely at 156°, but it immediately solidifies again and, if heated higher, begins to decompose a few degrees above this point. If a larger quantity of the salt is kept at 156°, it remains liquid for some time but ultimately solidifies to a horny mass, which is no longer soluble in alcohol. It was impossible to determine the nature of the change which takes place at this temperature, as no pure product could be isolated. If the temperature is kept sufficiently low there is no loss in weight; the product is colorless, reacts with bromine and permanganate in the cold, and gives off ammonia with alkalies.

The potassium salt was prepared by neutralizing the acid with potassium carbonate, evaporating to dryness, and crystallizing the residue from 95 per cent. alcohol.

I. 0.2125 gram of the air-dried salt gave 0.1271 gram K_2SO_4.

II. 0.1955 gram of the salt gave 0.1170 gram K_2SO_4.

	Calculated for $C_2H_5SO_3K$.	I.	Found. II.
K	26.71	26.75	26.88

The salt is very soluble in water, moderately soluble in boiling 95 per cent. alcohol, insoluble in absolute alcohol. From water it crystallizes in large plates, from alcohol in thin spear-shaped needles. It deliquesces in moist air.

The sodium salt was prepared like the potassium salt, which it resembles in crystal form and properties.

I. 0.2323 gram salt gave 0.1275 gram Na_2SO_4.

II. 0.2217 gram salt gave 0.1220 gram Na_2SO_4.

	Calculated for $C_2H_3SO_3Na$.	Found. I.	II.
Na	17.69	17.77	17.85

The barium salt was prepared by neutralizing the acid with barium carbonate and evaporating to crystallization. The salt is insoluble in alcohol. From water it crystallizes in minute needles, containing 1 molecule of water of crystallization, which is given off below 110°.

I. 0.4520 gram of the salt lost 0.0225 gram H_2O.

II. 0.3298 gram of the salt lost 0.0162 gram H_2O.

	Calculated for $(C_2H_3SO_3)_2Ba.H_2O$.	Found. I.	II.
H_2O	4.87	4.98	4.91

I. 0.2100 gram of the anhydrous salt gave 0.1394 gram $BaSO_4$.

II. 0.2567 gram of the anhydrous salt gave 0.1710 gram $BaSO_4$.

	Calculated for $(C_2H_3SO_3)_2Ba$.	Found. I.	II.
Ba	39.1	39.1	39.22

The lead salt was obtained by neutralizing the acid with lead carbonate and recrystallizing from cold water. It crystallizes in hard, lustrous prisms, which are difficultly soluble in cold water. It is impossible to drive off all the water of crystallization without decomposing the salt. The analyses of the hydrous salt lead to the formula $(C_2H_3SO_3)_2Pb.2H_2O$.

I. 0.3215 gram substance gave 0.2750 gram $PbSO_4$.

II. 0.1621 gram substance gave 0.1376 gram $PbSO_4$.

	Calculated for $(C_2H_3SO_3)_2Pb.2H_2O$.	Found. I.	II.
Pb	57.96	58.27	57.9

Ethylenesulphone chloride was prepared by treating the potassium salt, suspended in chloroform, with slightly more than the calculated quantity of phosphorus pentachloride. After the reaction, which takes place in the cold, was complete, the potassium chloride formed was removed by filtration, and the chloroform by distillation. As it was found that the chlorides of phosphorus could not be completely removed

by distillation, the residue was poured into ice-water and washed until free from phosphorus. It was then dissolved in ether, the ethereal solution dried by means of calcium chloride and, finally, purified by fractional distillation under diminished pressure.

The chloride is an oily liquid which cannot be distilled under atmospheric pressure. Under a pressure of 250 mm. it boils at 118°–120° with slight decomposition.

I. 0.2621 gram substance gave 0.2640 gram AgCl.
II. 0.2428 gram substance gave 0.2450 gram AgCl.

	Calculated for $C_2H_3ClSO_2$.	Found. I.	II.
Cl	24.91	24.9	25.0

When decomposed with boiling water the chloride gives ethylenesulphonic acid.

Transformations of Ethylenesulphonic Acid.

Oxidation.

The acid is oxidized with the greatest ease. It reduces acid, neutral, and alkaline permanganate solutions in the cold. In acid solution the reaction with permanganate is quantitative :

0.1120 gram of the potassium salt, dissolved in water and acidified with sulphuric acid, decolorized 46.3 cc. of a normal potassium permanganate solution (1 cc. = 0.016 gram oxygen, in acid solution), corresponding to 95.8 grams oxygen per molecular weight of salt.

0.2009 gram of the same salt decolorized 92.7 cc. of the permanganate solution, corresponding to 95.9 grams oxygen per molecular weight of salt.

The oxidation, therefore, takes place according to the equation :

$$C_2H_3SO_3H + 6O = 2CO_2 + H_2O + H_2SO_4.$$
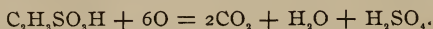
In acid and neutral solutions the reaction is instantaneous. In very strongly alkaline solutions it takes place more slowly, but the products are the same. Sulphuric acid can be detected in the liquid after a small quantity of permanganate has been added ; and, if the amount of permanganate added is insufficient for complete oxidation according to the equation given, a corresponding amount of substance can be recovered unchanged.

The ease with which the substance is oxidized is best seen in its behavior towards silver nitrate solution. If a quantity of the potassium salt is added to an ammoniacal solution of silver nitrate, and the liquid warmed until deposition of silver just begins, the reaction continues even after cooling, until all the salt is oxidized or all the silver deposited.

Many other methods of oxidation were tried in the hope of getting sulphoformic acid according to the equation:

$$\begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ SO_3H \end{array} + 5O = CO_2 + H_2O + \begin{array}{c} COOH \\ | \\ SO_3H \end{array}.$$
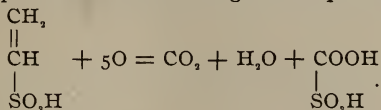
The result, however, was the same in all cases. All oxidizing agents which attack ethylenesulphonic acid destroy it completely, forming sulphuric acid, carbon dioxide, and water.

Reduction.

The acid is reduced with difficulty. Sodium amalgam, which reduces acrylic acid to propionic acid, seems to have no effect upon the analogous sulphonic acid. 50 cc. of a solution of the sodium salt, of such a strength that 1 cc. was capable of reducing 10 cc. of standard permanganate, was kept in contact with sodium amalgam for six days, then acidified and brought to known volume, when 1 cc. was found equivalent to 9.6 cc. of the permanganate solution. There was no reduction. 50 cc. of the same solution were then warmed with the sodium amalgam for five hours, when it was found that the solution no longer reduced permanganate. On concentrating the alkaline liquid a sodium salt crystallized out. This was purified by recrystallizing it from alcohol.

I. 0.3543 gram substance gave 0.2090 gram CO_2, and 0.1081 gram H_2O.

II. 0.2998 gram substance gave 0.1769 gram CO_2, and 0.0910 gram H_4O.

III. 0.1895 gram substance gave 0.0910 gram Na_2SO_4.

IV. 0.2110 gram substance gave 0.1015 gram Na_2SO_4.

	Calculated for $C_2H_5SO_4Na$.	I.	II.	III.	IV.
			Found.		
C	16.2	16.1	16.2	....	....
H	3.4	3.3	3.4	....	....
Na	15.54	....	....	15.55	15.79

The substance is not a reduction-product of ethylene-sulphonic acid; but a salt of oxyethanesulphonic acid formed by the addition of water to the unsaturated acid:

$$C_2H_3SO_3Na + H_2O = C_2H_4OHSO_3Na.$$
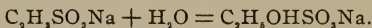
The filtrate from this salt was neutralized with sulphuric acid, concentrated and freed from most of the sodium sulphate by addition of alcohol. The filtrate from the sodium sulphate was evaporated to dryness, and extracted with alcohol. No other organic salt was present.

Attempts to reduce the acid with nascent hydrogen in acid solution met with no better success. A solution of the acid, of known reducing power, was boiled with zinc and dilute sulphuric acid for twenty hours without any appreciable change.

Ten gram portions of the acid were finally sealed up with hydriodic acid and phosphorus and heated to 170° for ten hours. After the iodine and hydriodic acid had been removed, in the usual way, the liquid was neutralized with potassium carbonate, evaporated to small volume and poured into alcohol. A potassium salt separated out and was purified by recrystallization from water.

I. 0.4365 gram substance gave 0.2580 gram CO_2, and 0.1335 gram H_2O.

II. 0.3576 gram substance gave 0.2100 gram CO_2, and 0.1124 gram H_2O.

III. 0.2108 gram substance gave 0.1245 gram K_2SO_4.

IV. 0.1898 gram substance gave 0.1116 gram K_2SO_4.

	Calculated for $C_2H_5SO_3K$.	Found.			
		I.	II.	III.	IV.
C	16.2	16.1	16.0	....	....
H	3.4	3.4	3.6	....	....
K	26.35	....	....	26.49	26.36

The salt has the composition and properties of potassium ethanesulphonate. For further identification it was treated with phosphorus pentachloride. The product, after purification, boiled at 171°—the boiling-point of the ethanesulphone chloride.

On concentrating the alcoholic solution a second salt was obtained. This, as shown by the analyses, was potassium oxyethanesulphonate:

I. 0.3015 gram substance gave 0.1598 gram CO_2, and 0.0825 gram H_2O.

II. 0.4522 gram substance gave 0.2410 gram CO_2, and 0.1507 gram H_2O.

III. 0.1521 gram substance gave 0.0802 gram K_2SO_4.

IV. 0.1155 gram substance gave 0.0612 gram K_2SO_4.

	Calculated for $C_2H_5SO_3K$.	I.	II.	Found. III.	IV.
C	14.6	14.4	14.3	....	....
H	3.04	3.4	3.0	....	....
K	23.7	....	....	23.6	23.7

These results show that when ethylenesulphonic acid is heated with hydriodic acid and phosphorus two reactions take place :

$$\text{I. } C_2H_3SO_3H + 2H = C_2H_5SO_3H.$$
$$\text{II. } C_2H_3SO_3H + H_2O = C_2H_4OHSO_3H.$$
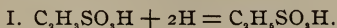
Addition of Water.

Aqueous solutions of ethylenesulphonic acid are quite stable at the boiling-point of water. Moderately concentrated solutions of the acid and of the potassium salt were boiled for ten hours without diminution in reducing power. The same solutions were then sealed up and heated to 150°. After heating for ten hours, the solutions no longer reduced permanganate in the cold. The acid was neutralized with potassium carbonate, the two solutions were evaporated to dryness, and the residues recrystallized from alcohol. The product in both cases was the potassium oxyethanesulphonate, which was obtained when the acid was heated with hydriodic acid.

In crystal form and solubility, the salt agrees closely with Liebig's description of potassium isethionate. Liebig states that potassium isethionate melts at 350° and does not lose water below this point. The potassium salt obtained by me melts sharply at 190° and loses water below 200°, passing into the anhydride, $C_4H_8S_2O_7K_2$.

I. 0.2240 gram salt gave 0.1265 gram K_2SO_4.

II. 0.2042 gram salt gave 0.1146 gram K_2SO_4.

	Calculated for $C_4H_8S_2O_7K_2$.	I.	Found. II.
K	25.2	25.3	25.2

When treated with phosphorus pentachloride the salt gave a chloride boiling at 200°, the boiling-point of (1,2)-chlorethanesulphone chloride.

I. 0.2167 gram substance gave 0.3828 gram AgCl.

II. 0.1850 gram substance gave 0.3255 gram AgCl.

	Calculated for $C_2H_4SO_2Cl_2$.	Found.	
		I.	II.
Cl	43.6	43.8	43.6

This could only have been formed from a (1,2)-oxyethane-sulphonic acid :

$$\begin{matrix} CH_2OH \\ | \\ CH_2SO_3K \end{matrix} + 2PCl_5 = \begin{matrix} CH_2Cl \\ | \\ CH_2SO_2Cl \end{matrix} + 2POCl_3 + HCl + KCl.$$
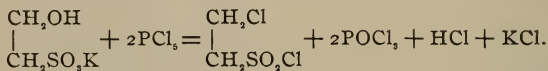
Hence, when ethylenesulphonic acid combines with water the hydroxyl group goes into the (2)-position with reference to the sulphoxyl group :

$$\begin{matrix} CH_2 \\ || \\ CHSO_3H \end{matrix} + \begin{matrix} OH \\ | \\ H \end{matrix} = \begin{matrix} CH_2OH \\ | \\ CH_2SO_3K \end{matrix}.$$
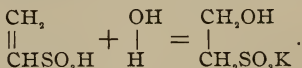
Since but one (1,2)-oxyethanesulphonic acid is theoretically possible, the experiments of Liebig were repeated. The potassium isethionate obtained melted at 190° and decomposed below 200°. The high temperatures observed by Liebig and Berzelius must have been due to some impurity introduced with the alcohol with which they started.

These experiments show that water can be added to ethylenesulphonic acid and its salts without the presence of other substances. The addition takes place much more readily in alkaline solution. If an alkaline solution of the potassium salt is boiled for a few hours, the salt is completely transformed into isethionate, and if a small quantity of alcoholic potash is added to an alcoholic solution of the same salt, the transformation takes place in the cold.

Addition of Hydrochloric Acid.

A quantity of the potassium salt was heated with concentrated hydrochloric acid for five hours at 130°. The resulting liquid was diluted until the potassium chloride that had separated was redissolved, then neutralized with lead carbonate and the filtrate from the lead chloride evaporated to

dryness. The residue contained two salts which were separated by fractional crystallization from alcohol. About 75 per cent. of the product was the potassium salt of (1,2)-chlor-ethanesulphonic acid,

$$\begin{matrix} CH_2Cl \\ | \\ CH_2SO_2K \end{matrix}.$$
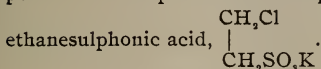
I. 0.1878 gram substance gave 0.1469 gram AgCl.
II. 0.1993 gram substance gave 0.1574 gram AgCl.
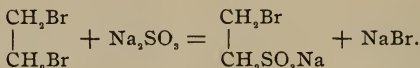III. 0.1629 gram substance gave 0.0771 gram K_2SO_4.
IV. 0.1941 gram substance gave 0.0930 gram K_2SO_4.

	Calculated for $C_2H_4ClSO_3K$.	I.	II.	Found. III.	IV.
Cl	19.45	19.36	19.55	....	....
K	21.36	....	....	21.21	21.46

The position of the chlorine atom was determined by treating the salt with phosphorus pentachloride, when (1,2)-chlorethane chloride, boiling at 200°, was obtained.

The second product was potassium isethionate, formed by the addition of water.

Addition of Hydrobromic Acid.

The addition of hydrobromic acid takes place under the same conditions as that of hydrochloric acid. The product is the potassium salt of (1,2)-bromethanesulphonic acid.

I. 0.2127 gram substance gave 0.1760 gram AgBr.
II. 0.2427 gram substance gave 0.2019 gram AgBr.
III. 0.1828 gram substance gave 0.0710 gram K_2SO_4.
IV. 0.3122 gram substance gave 0.1199 gram K_2SO_4.

	Calculated for $C_2H_4BrSO_3K$.	I.	II.	Found. III.	IV.
Br	35.24	35.25	35.47	....	....
K	17.18	....	....	17.4	17.22

The salt is readily soluble in water and alcohol. From water it crystallizes in orthorhombic tables, from absolute alcohol in thin, friable laminæ. To determine the position of the bromine atom the salt was boiled with silver oxide until all the bromine was replaced with hydroxyl. The product was potassium isethionate.

$$\begin{matrix} CH_2Br \\ | \\ CH_2SO_2K \end{matrix} + AgOH = \begin{matrix} CH_2OH \\ | \\ CH_2SO_2K \end{matrix} + AgBr.$$
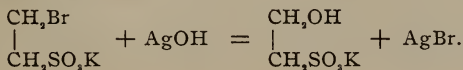
The sodium salt of the same bromethanesulphonic acid was obtained, in quantity, by slowly adding sodium sulphite to a boiling solution of ethylene bromide in water to which a small quantity of alcohol had been added. If the ethylene bromide is kept in excess, only one of its bromine atoms is replaced :

$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + Na_2SO_3 = \begin{array}{l} CH_2Br \\ | \\ CH_2SO_3Na \end{array} + NaBr.$$

The results of a detailed study of the acid will be published in a separate paper.

Reaction between Ethylenesulphonic Acid and Bromine.

Aqueous solutions of ethylenesulphonic acid rapidly decolorize bromine water in the cold. The result, however, is not addition but substitution. Hydrobromic acid can be detected in the liquid after a single drop of bromine has been added and, as the following results show, a molecule of hydrobromic acid is formed for every molecule of bromine that enters into reaction.

In the following experiments definite quantities of bromine were added to dilute solutions of the acid contained in measuring-flasks. After shaking until the color of bromine had disappeared, the solutions were brought to known volume and the hydrobromic acid determined volumetrically. As the bromine was drawn from burettes, and, as the last portions react very slowly, the results are not quite accurate. The calculations are based on the equation :

$$C_2H_3SO_3H + Br_2 = C_2H_2BrSO_3H + HBr.$$
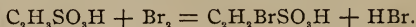
I. 1.549 grams bromine, added to an excess of the acid, liberated 0.7802 gram hydrobromic acid instead of 0.7841 gram calculated.

II. 2.425 grams bromine added to an excess of the potassium salt, liberated 1.250 grams hydrobromic acid instead of 1.228 grams calculated.

III. 2.0634 grams of the potassium salt reacted with 2.3592 grams bromine instead of 2.2606 grams calculated.

These results show that the above equation accurately expresses the course of the reaction. To isolate the organic

product of the reaction the hydrobromic acid was precipitated as lead bromide, the lead removed as sulphide, the acid thus obtained neutralized with potassium carbonate, and the solution evaporated to dryness. The residue was almost completely soluble in boiling absolute alcohol. On cooling the alcoholic solution a potassium salt separated in long colorless needles. The salt was washed with ether, dried at 50°, and analyzed.

I. 0.5135 gram substance gave 0.2051 gram CO_2, and 0.0411 gram H_2O.

II. 0.5288 gram substance gave 0.2075 gram CO_2, and 0.0431 gram H_2O.

III. 0.1907 gram substance gave 0.1598 gram AgBr.

IV. 0.1832 gram substance gave 0.1530 gram AgBr.

V. 0.2108 gram substance gave 0.2192 gram $BaSO_4$.

VI. 0.2122 gram substance gave 0.2190 gram $BaSO_4$.

VII. 0.1728 gram substance gave 0.0663 gram K_2SO_4.

VIII. 0.2601 gram substance gave 0.0998 gram K_2SO_4.

	Calculated for $C_2H_2BrSO_3K$.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C	10.66	10.86	10.72	....	....	....	....	....	....
H	0.88	0.93	0.98	....	....	....	....	....	....
Br	35.55	....	....	35.72	35.6	....	....	....	....
S	14.22	....	....	....	....	14.31	14.15	....	....
K	17.33	....	....	....	....	....	....	17.15	17.19

The salt cannot be crystallized from water. It is readily soluble in aqueous alcohol, moderately soluble in boiling, absolute alcohol. It is extremely hygroscopic, deliquescing rapidly in the air.

The structure of this substance is not yet determined with absolute certainty; but its properties are most easily explained on the assumption that it is a salt of (1)-bromethylenesulphonic acid,

$$\begin{matrix} CH_2 \\ \| \\ CBrSO_3H \end{matrix}$$

If a solution of the acid, or any of its salts, is shaken with a dilute solution of barium hydroxide, it is rapidly destroyed, the sulphonic acid residue being split off and precipitated as barium sulphite while the bromine remains in solution as bromide. From the solution ether extracts a substance which

on evaporation separates out as a gum insoluble in ether and alcohol, soluble in water. Every effort to obtain the substance in a form fit for analysis failed. In the air it hardens into a horny mass of variable composition. Silver oxide and cold permanganate have no action upon it, while hot acid permanganate oxidizes it to carbon dioxide and water. Nitric acid gives a small quantity of oxalic acid. The structure of a monobromethylenesulphonic acid must be either

$$\begin{array}{ccc}
CHBr & & CH_2 \\
\| & or & \| \\
CHSO_3H & & CBrSO_3H \\
\text{I.} & & \text{II.}
\end{array}$$
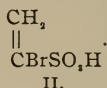
Since, on treatment with barium hydroxide, the bromine goes into solution as bromide, the primary action of the hydroxide is probably the replacement of bromine by hydroxyl. This, in the case of a substance with the formula I., ought to give a fairly stable sulphonic acid :

$$2\begin{array}{c} CHBr \\ \| \\ CHSO_3H \end{array} + Ba(OH)_2 = BaBr_2 + 2\begin{array}{c} CHOH \\ \| \\ CHSO_3H \end{array} \longrightarrow \begin{array}{c} CHO \\ | \\ CH_2SO_3H \end{array}.$$
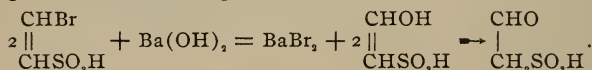
The same change in a substance with the structure represented by II., would give an arrangement that is known to be unstable :

$$2\begin{array}{c} CH_2 \\ \| \\ CBrSO_3H \end{array} + 2Ba(OH)_2 = \left(\begin{array}{c} CH_2 \\ \| \\ C{<}^{OH}_{SO_3} \end{array}\right)_2 Ba + BaBr_2.$$
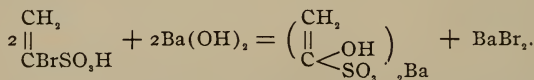
All (1,1)-oxysulphonic acids are readily decomposed by alkalies, the sulphonic acid group being split off as sulphite. With barium hydroxide a sulphonic acid, like the above, would be expected to react according to the equation :

$$\left(\begin{array}{c} CH_2 \\ \| \\ C{<}^{OH}_{SO_3} \end{array}\right)_2 Ba + Ba(OH)_2 = 2BaSO_3 + \begin{array}{c} CH_2 \\ \| \\ C=O \end{array} + 2H_2O.$$
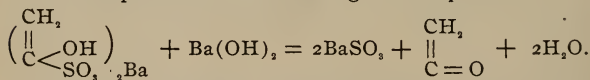
Formula II., therefore, explains the ease with which the sulphonic acid group is split off and also the formation of the gum obtained, as a substance with the structure $\begin{array}{c} CH_2 \\ \| \\ CO \end{array}$ would probably polymerize as fast as formed.

Summary.

The properties of ethylenesulphonic acid are, in the main, such as would be expected in a (Δ-1,2) unsaturated sulphonic acid. From the corresponding saturated acid it differs markedly, in its sensitiveness to reagents: it is easily oxidized, it combines with a number of substances, and it readily exchanges a part of its hydrogen for halogens and for acid groups.

Like most of the unsaturated carbonic acids, ethylene sulphonic acid instantly reduces a solution of permanganate. In its behavior towards oxidizing agents it differs from unsaturated carbonic acids, in that no intermediate oxidation-products are formed. All oxidizing agents, which attack the acid, completely destroy it, forming carbon dioxide, water, and sulphuric acid.

The acid is reduced with difficulty, sodium amalgam in alkaline solution, and zinc in acid solution, have no effect on it. When heated with hydriodic acid, however, it is reduced to ethanesulphonic acid.

Ethylenesulphonic acid readily combines with water and the halogen acids. In all cases the combination takes place in the same way as with (Δ-1,2) unsaturated carbonic acids— the negative component of the molecule added does not unite with the carbon atom which has the smallest number of hydrogen atoms in combination with it, but always goes into the (2)-position with reference to the sulphoxyl group.

The behavior of the acid towards bromine is peculiar. While the two react at all temperatures above the freezing-point of water, and in all solvents, the result is not addition but substitution. The product is (1,1-)bromethylenesulphonic acid. A similar result has been obtained with a few unsaturated carbonic acids. In these cases it is generally assumed that the first reaction is addition of bromine, and that this is followed by rearrangement and subsequent splitting off of hydrobromic acid. Such an assumption is not permissible in the present case because the dibromethanesulphonic acid, which would be formed by the addition of bromine to ethylenesulphonic acid can be prepared in a different way and is perfectly stable up to the boiling-point of water.

Chemical Laboratory, Bryn Mawr College.

NOTES.

Krypton, Neon, Metargon, and Coronium—Recently Discovered Constituents of the Atmosphere.

The discovery of rubidium and caesium by Bunsen and Kirchhoff by the use of the spectroscope opened up a new field for investigation and a study by this method of the solid constituents of the earth revealed several hitherto unknown elements. A more recent investigation, in the same general lines, of the gaseous envelope of the earth, all of whose constituents were supposed to have been isolated and identified, has led to equally surprising results. In the course of the study of argon and helium and attempts to purify them, three new gases have been isolated. An investigation carried on by Ramsay and others showed that no new gases could be obtained from the nitride of magnesium, formed in the preparation of argon; but a study of the residue from liquid air gave unexpected results. In a communication to the Royal Society,[1] Prof. Ramsay and Mr. Travers gave a preliminary notice of the isolation of a new gas. By allowing 750 cc. of liquid air to evaporate until only 10 cc. were left, collecting the gas from this and, after removing the oxygen and nitrogen, sparking over caustic soda with oxygen, they obtained 26.2 cc. of a gas which showed two spectra, a feeble argon spectrum and one which had not before been observed. This latter is characterized by the presence of two very brilliant lines, one almost identical with D_3 and another, a green line, comparable with the green helium line. Measurements by Mr. Baly show the presence of the following lines, all four of which are in the field at the same time:

$$D_1\ 5895.0, \quad D_2\ 5889.0, \quad D_3\ 5875.9, \quad D_4\ 5867.7.$$

The spectrum of this gas and that of argon were compared and the results were such as to characterize the gas as one before unknown. The density of the gas, taking the average of two determinations, was 22.49 if oxygen is taken as 16. The determination of the velocity of sound in the gas showed it to be, like argon and helium, monatomic, and of an elementary character. To this constituent of the atmosphere, which is heavier than argon and less volatile than nitrogen, oxygen and argon, they have given the name "krypton" (hidden).

In a later communication[2] to the Royal Society the same authors announce the discovery of two more constituents of atmospheric air. Dr. Norman Collie succeeded, by long-con-

[1] Proc. Royal Soc., **63**, 405.   [2] *Ibid.*, **63**, 437.

tinued diffusion, in separating argon into two portions, one with a density of 19.93 and the other with that of 20.21, a difference too slight to admit of any conclusion as to the presence of more than one substance.

By the liquefaction of large volumes of argon, using liquid air as the cooling agent, Ramsay and Travers have isolated two gases which they consider to be hitherto unknown elements. When argon was allowed to enter a bulb, cooled by liquid air, it formed a liquid; but at the same time a white solid appeared on the sides and in the liquid. After standing some time this mixture was allowed to evaporate slowly and fractions were taken off from time to time. The liquid evaporated off first and practically all of it could be removed before there was any marked change in the solid. The latter evaporated slowly, the last portion when the bulb was removed from the protecting jacket and the finger applied to the surface of the glass. The lighter gas which first evaporated had a density of 17.2, which decreased after further purification to 14.67 and, after a preliminary fractionation, to 13.7. In order to occupy the place in the periodic system which it would be expected to fill, it should have a density of 10 or 11, and the fact that the partial purification reduced the density from 17.2 to 13.7 gives hope of further reduction. An examination of the gas, after it had been sparked with oxygen, showed the presence of a number of bright red lines, a bright yellow one, and less conspicuous green and blue lines. The yellow line, although equal in intensity to the yellow lines of sodium, helium, and krypton, was found to have a different wave-length from any of these. This gas, to which they give the name "neon" (new), behaves in a vacuum-tube entirely differently from other known gases. It is rapidly absorbed by the red hot aluminium electrodes, and the color changes from a carmine-red to a brilliant orange.

The gas obtained from the white solid, after the liquid had boiled away, gave a spectrum which was entirely different from that of argon, although resembling it in general character. With low dispersion it gave a banded spectrum; but with a grating single, equidistant, bright lines appeared with the intermediate spaces filled with dim lines. The density of the gas is practically identical with that of argon, being 19.87, and it is monatomic. As the gas had a different spectrum from argon, and behaved differently at low temperatures, they concluded that it was elementary and called it "metargon." It holds the same position towards argon that nickel does to cobalt, having approximately the same atomic weight but dif-

ferent properties. They believed the absence of krypton from the high-boiling portion was due to the fact that in order to prepare it they would have had to use 60,000 times the amount of air they actually used, and then again while metargon is a solid, at the temperature of liquid air, krypton is probably liquid, and therefore more volatile. Moreover, the air from which the krypton was obtained had been filtered and so was freed from metargon.

Professor Schuster called attention to the fact that the spectrum of metargon showed great similarity to the spectrum of carbon, not in a few lines only, but throughout the whole visible spectrum. He thinks this a strong point against the dissimilarity of the two substances, and is not willing to accept this new element without further evidence. He thinks the spectroscopic evidence would indicate the presence of a compound of carbon mixed with argon or an unknown substance. Ramsay acknowledged the justice of Schuster's claim as to the great similarity of the two spectra, but decided as a result of further experiment that there was no evidence of the presence of carbon. He found that the gas had the same spectrum even after being sparked for two hours with oxygen; that no carbonic oxide bands could be found when the gas, mixed with oxygen, was introduced into a vacuum-tube and that a mixture of carbon monoxide and argon, after being sparked with oxygen, showed no carbon lines or bands. In hundreds of cases they have removed traces of carbon compounds by increasing the intensity of the current; but this had no effect here.

Professor Dewar says he has failed to see any signs of metargon in a sample of pure argon, which Lord Rayleigh had given him, which had been repeatedly liquefied, and he inquires as to the absence of the metargon of Ramsay and Travers. We thus see that while the presence of krypton and neon are fairly well established, more evidence is desired with regard to metargon.

Professor Nasini of Padua has been engaged for some time on a study of the gases emanating from the earth in various parts of Italy, and has already published some of the results obtained. In a brief note communicated to the French Academy, in July, he announced the discovery of a gas which had not been found before on the earth.

The gases from the Solfatara di Pozzuoli contained a gas which gave the wave-length 531.5, corresponding to that of corona 1474 K, attributed to an undiscovered element coronium, which should be lighter than hydrogen. The fumarole of Vesuvius also gave a gas with the same characteristic lines which are approximately those of various elements as iron and

potassium ; but these elements could not be present in the gas used.   One of the lines is very near one of the nitrogen lines ; but it cannot be due to nitrogen, as the other lines are not present. This gas to which the name coronium has been given was observed in the corona of the sun and was erroneously supposed, for a long time, to be present in the aurora borealis. It is lighter than hydrogen and cannot be a modification of any known element as it occurs at a distance of 300,000 miles from the body of the sun, and the lines are perfectly sharp and straight and never bent, as are those of all known elements, during solar disturbances.

The appearance of so many new elements at one time will no doubt prove embarrassing with the present arrangement of the Periodic System, and attempts will probably be made to re-arrange the system to conform to these new discoveries.   Professor Crookes has suggested an arrangement of the elements in the form of a double spiral in which the elements are ar-ranged in three dimensions in space, the three elements dis-covered by Ramsay falling in the vertical column under he-lium between the hydrogen family, containing chlorine, bro-mine and iodine, and the lithium family.   J. E. G.

Fermentation without Cells.

Eduard Buchner delivered a lecture on this subject before the German Chemical Society, March 14, 1898, and an abstract of the lecture was published in the *Berichte*, April 25, 1898. In view of the importance of the results reached and described by Buchner, a brief account of the work is here given.

As is well known the investigations of Pasteur led to the conclusion that the process of fermentation necessarily involves the action of organisms.   Pasteur regarded fermentation as a physiological act, closely and inseparably connected with the vital phenomena of the yeast cells.   Other investigators, on the contrary, as Moritz, Traube, Berthelot, Liebig, and Hoppe-Seyler, were of the opinion that the yeast produces a substance which effects fermentation just as it produces a definite chemical substance, an unorganized ferment or enzyme, *invertase*, which splits cane-sugar into grape-sugar and fruit sugar.   But this theory lacked experimental basis. The vitalistic theory of Pasteur, therefore, prevailed.

Buchner, in October, 1896, first obtained evidence that fermentation can be effected without cells, but doubted his results.   Further work showed, however, that a liquid free from cells can be expressed from yeast which liquid can cause the fermentation of sugar.

The process by which the liquid is obtained is the following :

Fresh Munich low-fermentation beer press-yeast, dehydrated under a pressure of 50 atmospheres, is mixed with its own weight of quartz sand and a fifth of its weight of infusorial earth, and then thoroughly triturated. The process is interrupted only when the mass, which at first forms a dry powder, of itself becomes moist. Now, the dough-like mass, wrapped in a cloth, is subjected to a pressure of 500 atmospheres. In about two hours the cake is broken up, moistened with water, and again subjected to the same high pressure. From 1 kilogram yeast about 500 cc. liquid is obtained, and of this 140 cc. is water that has been added. The liquid from the press is allowed to drop directly upon a fluted filter and is collected in a vessel cooled to 0° by ice-water in order, as far as possible, to prevent any change of the liquid during the preparation.

The fresh yeast juice is a yellowish liquid, which appears almost clear by transmitted light, but is otherwise opalescent. It has a pleasant odor of yeast, and contains much carbon dioxide in solution. A considerable quantity of coagulable albumin is present in it. Enzymes are also present in the yeast juice. Of these, invertase has been identified. The presence of maltase and of a ferment capable of hydrolyzing glycogen appears probable. Proteolytic enzymes have been found in the juice by M. Hahn.

The most interesting property of the yeast juice, however, is its power to cause the alcoholic fermentation of sugars. Like yeast itself, it affects cane, malt, grape, and fruit sugars, but not lactose and mannite.

From all the numerous experiments that have thus far been made, the conclusion is drawn that the living yeast cells are not necessary to the process of alcoholic fermentation. The phenomenon of fermentation is not, therefore, to be regarded as a physiological act. It is rather brought about by an enzyme-like substance, *zymase*, which is only formed in nature in the living yeast cell. This substance cannot yet be isolated, on account of its instability, and the presence of other enzymes.

Buchner takes up the objections that have been raised against his conclusions, but makes it appear clear that these are not justified.   I. R.

AMERICAN

CHEMICAL JOURNAL

CVIII.—ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.[1]

By Theodore William Richards.

In a recent critical discussion of Stas' work upon the atomic weight of carbon, Dr. Alexander Scott,[2] of London, had occasion to repeat some observations made at Harvard several years ago.[3] According to these observations, cupric oxide made from cupric nitrate had been found usually to contain several times its volume of occluded gases, chiefly nitrogen, and moreover it was shown that this gas resulted from the decomposition of minute traces of residual nitrate confined in the inmost recesses of the masses of oxide. Dr. Scott, however, could not find as much as one-tenth of this amount of gas in his material. Since he was unable to explain the apparent discrepancy, it is one of the objects of the present paper to shed a clearer light upon the subject.

The essential point which escaped Dr. Scott's notice is this: the temperature of ignition is the most important condition determining the amount of the occluded gases. When the

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[2] J. Chem. Soc. Trans., **71**, 559, (1897).
[3] Proc. Am. Acad., **26**, 281 ; Ztschr. anorg. Chem., **1**, 196.

temperature is very high, nearly all of the imprisoned impurity is set free. To quote Dr. Scott's words, his oxide was exposed ''for varying times to a full red heat in a muffle heated with gas.'' It is well known that at a temperature of about 1000°, cupric oxide melts with a very considerable loss of oxygen. It is obvious, then, that temperatures in this neighborhood are quite out of the question when the atomic weight of copper is concerned ; and this constant was the chief subject of the old investigation. Hence, among the many experiments made by me in 1891, only three dealt with material which had been heated above 700°. The evidence of these three experiments (Nos. 59, 81, and 95), is unanimous in showing that most of the occluded impurity is set free at bright redness, and the first two of them agree quantitatively with the results of Dr. Scott.

Although it is thus evident that the English and American results are in no way inconsistent, I decided to repeat a part of the work, in order to obtain a more certain estimate of the various temperatures corresponding to the varying conditions of the cupric oxide. In my previous paper the higher degrees had been merely guessed, for they were not directly concerned in the point then under consideration.

The usual modes of determining high temperatures,—the calorimeter, the air-thermometer, the bolometer, the meldometer, the platinum-iridium thermopile, etc.,—are somewhat troublesome to use for a brief series of experiments of the present kind, so that it seemed best to determine the several temperatures approximately by finding, for each temperature, two substances whose melting-points were respectively above and below the point in question. For instance, an intensity of heat which would melt pure argentic bromide but not pure argentic chloride must be between 427° and 451°, a grade of accuracy more than sufficient for the present purpose.[1] This method of determining the temperature has the great advantage of providing an approximate self-registering thermometer, occupying very small space and needing no connection with

[1] Of course this idea is no new one. It has not often been used so systematically as in the present case, however.

the outside air. The usefulness of the method obviously depends upon the number of substances easily obtained in a pure state, whose melting-points are accurately known. For such knowledge of high melting-points we depend mainly upon four researches,—those of Carnelley,[1] Le Chatelier,[2] Meyer, Riddle, and Lamb,[3] and Ramsay and Eumorfopoulos.[4] Unfortunately the results of these four investigations do not always agree, their disagreement affording evidence of the great difficulty of measuring accurately high temperatures. At first sight the fact of the existence of such discrepancy might deter one from adopting this standard of reference, but further consideration leads to exactly the opposite conclusion. The melting-points of pure salts must be an unchangeable standard, and the uncertainty of our knowledge regarding them must be largely due to experimental difficulties in the thermometric manipulation. These difficulties, if so serious in researches where everything was favorable to accuracy, must be largely augmented in a research like the present one, in which the temperature could not be made the sole issue of the experiment. Hence the melting-point of a pure salt is the safest possible standard. The following table gives in parallel columns the salts chosen for the present scale of temperature, with the results of the four investigations, and the values of the melting-points selected as the most probable.

1 Carnelley : J. Chem. Soc., **29**, 489, **33**, 273, (1876 and 1878).

2 Le Chatelier : Bull. Soc. Chim., **47**, 300, (1887).

3 V. Meyer, Riddle, and Lamb : Ber. d. chem. Ges., **27**, 3129, (1895).

4 Ramsay and Eumorfopoulos : Phil. Mag., (5) **41**, 360, (1896).

Temperature Scale.

	Carnelley calorimeter.	Le Chatelier thermopile.	Meyer air therm.	Ramsay meldometer.	Value selected.
Potassic	339	...	...	339	339
AgI,2AgBr,2AgCl	383	...	...	...	383
Argentic bromide	427	...	...	426	427
Argentic chloride	451	...	...	460	451
Plumbic chloride	498	...	...	447	498
Argentic iodide	527	...	...	556	529
Sodic biborate	561	...	...	...	561
Lithic chloride	598	...	...	491	598
Thallous sulphate	632	...	...	...	632
Strontic nitrate	645	...	...	570	645(?)
Potassic bromide	699	...	722	733	720
Potassic chloride	734	740	800	762	760
Sodic chloride	772	775	815.4	792	790
Sodic carbonate	814	810	849	851	830
Strontic chloride	825	840	832	796	835 (?)
Sodic sulphate	861	867	863	884	865
Baric chloride	860	...	921	844	920 (?)
Potassic sulphate	...	1045	1078	1052	1060

The most serious discrepancies are to be noticed in the cases of potassic and sodic chlorides, where the respective averages have been chosen as the most probable values. These averages are almost identical with the figures obtained by Ramsay and Eumorfopoulos. On the other hand, Joly's meldometer, used by these investigators, seems to have been much less satisfactory at lower temperatures ; for their melting-points of plumbic chloride and lithic chloride are widely different from Carnelley's. Repeated qualitative experiments have convinced me that plumbic chloride is less easy to melt than argentic chloride, and lithic chloride less easy to melt than argentic iodide ; therefore Carnelley's calorimetric results have been adopted here as the more accurate. Strontic nitrate, and strontic and baric chloride all begin to decompose in the air at or near their melting-points ; undoubtedly this fact is responsible for the very low results obtained by Ramsay and Eumorfopoulos in these cases. Obviously such salts cannot be relied upon as trustworthy thermometers, un-

less one takes the precautions observed by Meyer, Riddle, and Lamb in their work with the air thermometer. One is reminded of the interesting work of Hill upon changeable organic melting-points.[1] The other substances in the list are sufficiently stable, and are easily obtained in a pure state. In the light of Le Chatelier's complete confirmation of Carnelley's results by means of the pyrometric thermopile, it is odd that the lamented Victor Meyer accorded Carnelley so little credit as he has done.

It is needless to state that pains was taken to eliminate impurities from these substances by recrystallization or other suitable means, and to dry the salts thoroughly, in the work which follows. If the temperature was below 800°, the dry coarsely powdered substances were contained in small melting-tubes of the hardest Jena glass, sealed while hot at both ends, and sometimes provided with a small platinum sinker to show whether or not the salt had liquefied. If, on the other hand, the height of the temperature excluded glass, the substances were contained in small cups beaten into stout strips of platinum foil. The small amount of impurity taken from the glass tubes in which some of the substances were melted could hardly have had much effect on the melting-point until after a considerable mass of the substances had been melted; but then their mission had been fulfilled.

The table above might well be amplified to cover a wider range, as well as smaller differences of temperature, but such an amplification would constitute a research of some magnitude in itself. For present purposes the above will suffice.

Two forms of apparatus were used for determining the amount and the composition of the occluded gases. The first was identical in every respect with the most convenient of the three forms described in the original paper.[2] It consists of several bulbs blown in the bend of a glass tube bent at a right angle. One arm of the tube is temporarily closed by a stopcock (not shown in the cut in the original paper, although mentioned in the letterpress), and in this arm the gas evolved in the bulbs by the solution of the cupric oxide in acid, is collected and measured over boiled water. When necessary the gas

[1] H. B. Hill, Proc. Am. Acad., **23**, 219.　　[2] Proc. Am. Acad., **26**, 284, (1891).

may be readily removed through the stopcock at the end of the arm ; if a gas burette is attached here, of course the gas may be analyzed at once without further trouble.

For most of the experiments, however, Scott's modification of another of the original forms[1] was used. The mode of operating this apparatus was essentially similar to the method just described, although the bent tubes and bulbs are replaced by a small flask and funnel-tube. Scott's addition of a side tube to remove the displaced water distinctly increases the convenience and accuracy of the contrivance. For the details his paper should be consulted.

The two pieces of apparatus give identical results, which cannot be far from the truth. If at all in error the amount of gas collected must be too small rather than too large, for both oxygen and nitrogen are slightly soluble in water. This consideration was verified by fusing a specimen of oxide (another portion of which had been repeatedly analyzed in the usual fashion) with carefully prepared acid potassic sulphate in a Sprengel vacuum. The amount of gas evolved by this treatment was slightly greater, but only slightly greater than the amount obtained by the usual method, and its composition was essentially identical with that of the gas collected over boiled water. Since the question is one of relation, rather than of absolute values, the method involving the use of aqueous solutions was adopted because of its far greater ease of execution. Pains was taken to have the conditions of the solution of the oxide always as nearly as possible the same, so that the results should be strictly comparable with one another.

The first object of the present paper is to show more clearly the relation between the amount of gas retained by the oxide and the temperature used in its ignition. The material employed in these experiments was prepared by dissolving pure copper wire or electrolytic copper in pure nitric acid, and gradually converting by heat the crystallized cupric nitrate, finally into oxide.[2] Platinum vessels were used throughout,

[1] Proc. Am. Acad., **26**, 285, middle of page.

[2] It is interesting to note that the hydrate of cupric nitrate, which crystallizes from hot solutions, probably has the formula $3Cu(NO_3)_2.8H_2O$ (analogous to cadmic sulphate), not $Cu(NO_3)_2.3H_2O$ (Graham), as is usually supposed. Following are the

whenever heating was necessary, excepting that one or two of the first ignitions were conducted in a porcelain boat. Three preparations of the oxide were made ; one by the rapid decomposition of the nitrate, another by more gradual application of heat, and a third by the very slow action of a temperature just barely sufficient to effect the desired change. This temperature had been found previously by a special experiment to be about 280°, if the products of the decomposition remain in contact with the cupric oxide. The first of these preparations was the most coherent, and was capable of retaining the most gas ; the second was less coherent and retained less gas ; and the last was the most powdery and retained even less gas. Thus it is manifest that the physical condition of the solid is a factor in the question.

These specimens of the oxide of copper were subsequently ignited at varying temperatures for varying lengths of time in two different forms of furnace. For the first series a large tube or small muffle of Berlin porcelain capable of being heated to 1200° or more in a Fletcher furnace was used, but since it was found difficult to maintain the tube at a constant temperature throughout, this arrangement was later abandoned. All the subsequent ignitions were performed in a double crucible arranged in the manner shown in the diagram, the low platinum crucible or capsule used to contain the cupric oxide being protected from radiation and convection by a number of superimposed crucible lids. The outer glazed porcelain crucible and the layers of asbestos board covering the draught holes united in excluding the products of com-

analyses of three separate preparations, dried over moist potash (which does not dehydrate the crystals at ordinary temperatures), proving this point.

(1) 0.1739 gram of crystals yielded 0.0471 gram of copper = 27.08 per cent.
(2) 0 6310 " " " 0.1705 " " = 27.01 "
(3) 1.2897 " " " 0.3448 " " = 26.73 "

Average = 26.94 "

Theoretical value for $Cu(NO_3)_2.3H_2O = 26.20$ per cent. of copper.
" " $3 Cu(NO_3)_2.8H_2O = 26.98$ " "
" " $2 Cu(NO_3)_2.5H_2O = 27.35$ " "

The crystals analyzed in No. 3 above were large and undoubtedly contained included mother-liquor. Whether or not other hydrates exist, and what the transition temperatures may be, I did not take the trouble to discover. Much of our present data regarding water of crystallization has been rounded off in the manner indicated above. Undoubtedly many more such irregular ratios as 3 : 8 really exist than we are prepared at present to believe.
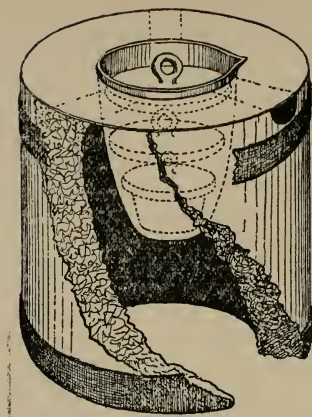
bustion of the illuminating gas from the contents of the inner capsule. By means of this furnace, fed with a constant gas supply burning from a fourfold Bunsen burner, a surprisingly constant and uniform temperature may be maintained for an indefinite length of time.

In the following table are given the new series of results showing the relation of the total volume of gas retained to the temperature used in the ignition of the cupric oxide. The gas volumes are reduced to 0° and 760 mm. pressure, the reduction having been made by means of a Winkler-Lunge corrector arranged to give directly the exact volume of a mass of moist air which would measure a hundred cubic centimeters when dry and under standard conditions.

THE EFFECT OF TEMPERATURE ON THE TOTAL AMOUNT OF GAS OCCLUDED BY CUPRIC OXIDE.

First Series : First Preparation of Cupric Oxide.

	Cc. gas.
1. 1 gram CuO, heated 1 hour at 300° ±,[1] gave	0.18
2. 1 gram CuO, heated 1 hour at 300° ±, gave	0.19
3. 1 gram CuO, heated 1 hour at 300° ±, gave	0.21
Average	0.19

[1] Mercury thermometer.

4.	1 gram CuO, heated 4 hours at 500° $\pm$,[1] gave	0.69
5.	1 gram CuO, heated 4 hours at 200° $\pm$, gave	0.72
	Average	0.70
6.	1 gram CuO, heated 1 hour at 830° $\pm$,[2] gave	0.68
7.	1 gram CuO, heated 1 hour at 830° gave	0.69
8.	1 gram CuO, heated 1 hour at 830° gave	0.68
	Average	0.68
9.	1 gram CuO, heated $\frac{1}{2}$ hour at 870° $\pm$,[3] gave	0.55
10.	1 gram CuO, heated $\frac{1}{2}$ hour at 900° $\pm$,[4] gave	0.08
11.	1 gram CuO, heated $\frac{1}{2}$ hour at 950° $\pm$,[5] gave	0.05
12.	1 gram CuO, heated $\frac{1}{2}$ hour at 950° $\pm$, gave	0.04
	Average	0.05
13.	1 gram CuO, heated $\frac{1}{2}$ hour at 1100° $\pm$,[6] gave	0.01(?)

Second Series : Second Preparation of Cupric Oxide.

14.	1 gram CuO, heated 4 hours at 280° $\pm$,[7] gave	0.04
15.	1 gram CuO, heated 1 hour at 290° $\pm$,[7] gave	0.12
16.	1 gram CuO, heated 5 hours at 630°,[8] gave	0.54
17.	1 gram CuO, heated 3 hours at 830°,[9] gave	0.57
18.	1 gram CuO, heated 3 hours at 830°, gave	0.59
19.	1 gram CuO, heated 5 hours at 830°, gave	0.57
	Average	0.58
20.	1 gram CuO, heated 20 minutes at 870° $\pm$,[9] gave	0.42
21.	1 gram CuO, heated 150 minutes at 870° $\pm$, gave	0.23
22.	1 gram CuO, heated 150 minutes at 870° $\pm$, gave	0.14
23.	1 gram CuO, heated 2 hours at 950° $\pm$,[9] gave	0.04
24.	1 gram CuO, heated 2 hours at 950° $\pm$, gave	0.07
25.	1 gram CuO, heated 2 hours at 950° $\pm$, gave	0.04
	Average	0.05

[1] Plumbic chloride just fused; argentic iodide remained solid.

[2] Sodic chloride easily fused; strontic chloride just fused; sodic sulphate remained solid.

[3] Sodic sulphate just fused.

[4] Sodic sulphate easily fused; higher than last.

[5] Baric chloride easily fused; potassic sulphate remained solid.

[6] Potassic sulphate fused, as well as the cupric oxide itself.

[7] Mercury thermometer.

[8] Thallous sulphate just melted.

[9] See foot-notes to preceding series for criteria regarding temperatures 830°, 870° and 950°.

These two series of experiments, qualitatively and quantitatively similar to those carried out in 1891, lead to the following conclusions, which are copied verbatim from the paper on the atomic weight of copper :—

" First, *that cupric oxide prepared by the ignition of the oxynitrate after Hampe's method contained between four and five times its volume of occluded gas.*

" Second, *that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was, nevertheless, considerably above that which Hampe apparently employed.*"

The recent experiments add to these conclusions only greater definiteness. It is now clear that nearly all the gas is retained until a temperature of slightly over 850° is reached, when more than 0.9 of it is rapidly set free. Somewhat above this point the cupric oxide is itself partly decomposed ; and in the neighborhood of 1000° the mixture of cupric and cuprous oxides fuses first into a mass resembling scoria, and then into a limpid fluid. It is evident that Scott must have used in his muffle a temperature somewhere between 850° and 1000°, for he found on the average 0.055 cc. of gas per gram of cupric oxide, while my results obtained by means of temperatures in this neighborhood average 0.05 cc. Moreover, some of his material was slightly reduced, but apparently none of it was melted.

It was clearly shown in the previous papers that the low results given by material ignited at temperatures below 450° are due to the presence of undecomposed cupric nitrate, which by its decomposition at higher temperatures yields the gas forming the subject of the present discussion.

The fact that prolonged ignition does not affect the amount of gas occluded may be inferred from the experiments just recorded ; but, in order to obtain more definite information on this influence of time, a third series of experiments was made.

THE EFFECT OF TIME OF IGNITION ON THE TOTAL AMOUNT
OF GAS OCCLUDED BY CUPRIC OXIDE.

Temperature : The Fusing-Point of Thallous Sulphate, about
640°.

	Cc. gas.
26. 1 gram of CuO, after ignition for 10 minutes, gave	0.56
27. 1 gram of CuO, after ignition for 10 minutes, gave	0.57
28. 1 gram of CuO, after ignition for 10 minutes, gave	0.53
Average	0.55
29. 1 gram of CuO, after ignition for 5 hours, gave	0.56
30. 1 gram of CuO, after ignition for 5 hours, gave	0.59
Average	0.57
31. 1 gram of CuO, after ignition for 20 hours, gave	0.56
32. 1 gram of CuO, after ignition for 20 hours, gave	0.59
Average	0.57

A portion of the last specimen, which had been heated for
twenty hours, was further ignited for five hours at about the
fusing-point of common salt (about 800°). Upon solution in
acid this portion yielded the same amount, 0.59 cc. of gas.
Thus another of the conclusions arrived at in 1892 is con-
firmed.

" Third, *that beyond a certain limit the time of ignition makes*
no important difference."

This is true, however, only below 850°. Experiments 20 to
22 show that when the imprisoned gas has once begun to be
set free, at temperatures above 850°, the time is an essential
factor ; and that when sufficient time has been allowed, the
expulsion of the gas is almost complete. Scott examined
only cupric oxide from which he had thus expelled nearly all
the gas, hence it is not surprising that he found very little.

In this connection it is interesting to note that Morse and
Arbuckle[1] have recently verified, with apparatus far more
elaborate and exact than ours, the results of Rogers and my-
self concerning the amount of gas occluded by the oxide of
zinc.[2] Considering the fact that the manner of preparation of

[1] This JOURNAL, **20,** 195. [2] *Ibid.,* **15,** 567.

the substance undoubtedly affects the amount of gas retained, the closeness of the agreement is surprising. Only one of their conclusions is different from ours: in their opinion, there is no reason to believe that the temperature of ignition of the oxide has any effect on the *composition* of the occluded gas, while in our experiments the imprisoned oxygen decreased with increasing temperature. The basis of their reasoning is the supposition that the total amount of gas retained is dependent solely upon the temperature; using this total amount as a thermometer, they point out the fact that the smaller amounts of gas obtained in their experiments did not always contain the smaller amounts of oxygen; and hence they conclude that the temperature is not an essential determining cause of the composition of the mixture. In a letter answering some questions about the matter, Professor Morse kindly writes, '' We made every effort to secure constant temperatures for our oxide, giving the closest attention, to that end, to every detail of the firing of the furnace, the fuel, the location of the crucibles,'' etc. Since this is the case, and I cannot doubt the essential success of their efforts, it seems to me that their results have but little bearing upon the effect of *varying* temperatures on the oxide. The fact that their mixture of gases was by no means constant in composition is better explained by the supposition that some other cause besides the temperature influences the relation of the volumes of oxygen and nitrogen retained, or else that the total amount of the enclosed gases is not a safe measure of the temperature. It will be shown that both of these inferences are correct, and hence that the logic of Morse and Arbuckle's point, correct in itself but unsafe in its premises, falls to the ground.

A careful study of all the data, Morse and Arbuckle's, as well as ours, convinced me that, while the two gases must be evolved together, they behave subsequently in quite a different fashion. It is apparent immediately that the oxygen must escape at first much faster than the nitrogen, for the ratio of the two volumes in the nitric anhydride set free must be originally 5 : 2, while the average of Morse and Arbuckle's result showed that less than a fifth of the finally retained mixture consisted of oxygen. Part of the loss might be due to

the preliminary formation of lower oxides, and to unequal diffusion, but this cannot account for so great a loss of oxygen. Even nitrous oxide should yield upon decomposition a mixture one-third of the volume of which must consist of oxygen; and the fractional diffusion of this mechanically enclosed mixture should allow the lighter of its two constituents, nitrogen, to escape the more quickly of the two; hence, the mixture should contain never less than thirty-three per cent. of oxygen. The same anomaly is even more manifest in the case of cupric oxide, for from this substance nearly all the oxygen soon escapes, even at comparatively low temperatures.

Why then does the oxygen escape the more easily of the two gases? This question introduces us at once to the second section of the paper, which deals with the composition of the occluded gases.

The first step toward answering the question is a certain determination of the facts, which have been doubted by Morse and Arbuckle. The three conditions which would be most likely to affect the amount and composition of the gaseous mixture are the temperature of ignition, the time of ignition, and the compactness of the solid material. In order to test the effect of these possible modifying causes experimentally, several series of analyses were made, both with zincic and with cupric oxide.

The zincic oxide was made by heating pure zincic nitrate for a long time at 280°. It was more compact than the cupric oxide, and undoubtedly contained residual traces of nitrate until further ignited.

THE EFFECT OF TEMPERATURE ON THE TOTAL VOLUME OF
GAS OCCLUDED BY ZINCIC OXIDE.

First Series : Heated Three Hours.

Cc. gas.

34. 1 gram of ZnO, after heating 3 hours at **660°**±, gave 0.365
35. 1 gram of ZnO, after heating 3 hours at **660°**±, gave 0.380

Average 0.373

36. 1 gram of ZnO, after heating 3 hours at **750°**±, gave 0.233
37. 1 gram of ZnO, after heating 3 hours at **750°**±, gave 0.210

Average 0.221

38. 1 gram of ZnO, after heating 3 hours at 880°±, gave 0.14
39. 1 gram of ZnO, after heating 3 hours at 880°±, gave 0.18

<div align="right">

Average   0.16
</div>

Second Series : Heated Thirty Minutes.

40. 1 gram of ZnO, after heating $\frac{1}{2}$ hour at **750°**±, gave 0.366
41. 1 gram of ZnO, after heating $\frac{1}{2}$ hour at **750°**±, gave 0.320

<div align="right">

Average   0.343
</div>

42. 1 gram of ZnO, after heating $\frac{1}{2}$ hour at **880°**±, gave 0.192
43. 1 gram of ZnO, after heating $\frac{1}{2}$ hour at **880°**±, gave 0.192

<div align="right">

Average   0.192
</div>

Evidently, other conditions being equal, the total amount of gas retained decreases very considerably as the temperature of ignition is raised. Each one of these specimens of gas was analyzed, by means of Hempel's apparatus modified for use on a small scale,[1] with interesting results. The actual volume of *nitrogen* in every gram of material was found to be

FIGURE 2.

almost identical, diminishing only very slightly, if at all, as the temperature increased, and amounting to about 0.14 cc. Thus the large differences in the total volumes are due almost wholly to *oxygen*, which varied from over 60 per cent. in the first average, to less than 20 per cent. in the third. The small amount of carbon dioxide present was absorbed almost completely by the boiled water over which the gases were collected, hence it need not be considered.[2] The actual volumes of nitrogen in the five averages were respectively 0.138, 0.133, 0.130, in the first series, aud 0.152 and 0.127 in the second series, while the actual amounts of oxygen were re-

[1] The most important modification was the arrangement for connecting pipette to burette. By blowing and drawing down the capillary it may be made to fit so perfectly into the fine rubber tube as to make the loss of small bubbles impossible. The diagram will make the idea clear (Fig. 2).

[2] This JOURNAL, **15**, 572. In a number of cases where pains was taken to measure the carbon dioxide, its volume never exceeded 3 or 4 per cent., and was usually about 2 per cent.

spectively 0.235, 0.087, 0.030 in the first series, and 0.191 and 0.065 in the second. No better proof could be desired of the fact that zincic oxide allows its oxygen to depart more easily than its nitrogen. These results are wholly confirmatory of the results of Richards and Rogers, already mentioned ; but, of course, they do not explain how Morse and Arbuckle, working at nearly constant temperature, obtained inconstant results. To accomplish this explanation, the other possible causes affecting the retention of gases must be considered.

THE EFFECT OF TIME OF IGNITION ON THE AMOUNT OF GAS RETAINED BY ZINCIC ACID.

First Series : Just above the Melting-point of Thallous Sulphate.

		Cc. gas.
44. 1 gram of ZnO, heated at **660°** for **1** hour, gave		0.46
34. 1 gram of ZnO, heated at **660°** for **3** hours, gave		0.36
35. 1 gram of ZnO, heated at **660°** for **3** hours, gave		0.38

Average 0.37

Second Series : Just above the Melting-point of Potassic Chloride.

45. 1 gram of ZnO, heated at **750°** for **10** minutes, gave 0.27
46. 1 gram of ZnO, heated at **750°** for **20** minutes, gave 0.35
40. 1 gram of ZnO, heated at **750°** for **30** minutes, gave 0.37
41. 1 gram of ZnO, heated at **750°** for **30** minutes, gave 0.32

Average 0.35

47. 1 gram of ZnO, neated at **750°** for **60** minutes, gave 0.30
48. 1 gram of ZnO, heated at **750°** for **60** minutes, gave 0.32

Average 0.31

36. 1 gram of ZnO, heated at **750°** for **180** minutes, gave 0.21
37. 1 gram of ZnO, heated at **750°** for **180** minutes, gave 0.25

Average 0.23

Third Series : Just above the Melting-point of Sodic Sulphate.

49. 1 gram of ZnO, heated at **880°** for **3** minutes, gave 0.49
50. 1 gram of ZnO, heated at **880°** for **5** minutes, gave 0.35
51. 1 gram of ZnO, heated at **880°** for **12** minutes, gave 0.29
52. 1 gram of ZnO, heated at **880°** for **12** minutes, gave 0.25

Average 0.27

42. 1 gram of ZnO, heated at 880° for 30 minutes, gave 0.19
43. 1 gram of ZnO, heated at 880° for 30 minutes, gave 0.19

Average 0.19

38. 1 gram of ZnO, heated at 880° for 180 minutes, gave 0.14
39. 1 gram of ZnO, heated at 880° for 180 minutes, gave 0.18

Average 0.16

In each of the series the same fact may be noted—the fact that continued heating at any one temperature is capable of causing a slow evolution of gas from the oxide. Only in the second of these series is evident an initial increase in the amount of gas, indicating a maximum after less than twenty minutes of heating. This increase, which is manifestly due to the advancing decomposition of the traces of imprisoned nitrate, undoubtedly ceases after an hour's heating at 660°, or after three minutes' heating at 880°; hence it does not appear in the first and third series.

The steady loss of gas after this maximum has been attained—a loss increasing with time as well as with increasing temperature in the case of *zincic* oxide—is worthy of further attention, especially because it will be remembered that the amount of gas retained by *cupric* oxide remained almost constant until a very high temperature was reached. Analysis of the several specimens of gas showed at once wherein lay the explanation; for they showed as before that the maximal quantities of gas consisted chiefly of oxygen; while the gas obtained by the last two experiments consisted chiefly of nitrogen. Here, again, the nitrogen remained nearly constant, only diminishing from 0.20 cc. at the maxima to about 0.13 cc. at the minima , while the oxygen diminished in the same samples from 0.21 to 0.03 cc.

It remains only, as far as zincic oxide is concerned, to show how wide a difference in the amount of gas may be caused by the original mode of preparation of the solid material.

THE EFFECT OF PHYSICAL CONDITION UPON THE TOTAL
AMOUNT OF GAS RETAINED BY ZINCIC OXIDE.

Cc. gas.

53. 1 gram of ZnO, prepared from zincic carbonate
at 880°, gave   0.00

54. 1 gram of ZnO, prepared from zincic carbonate
at 880°, gave   0.00
                                                      ─────
                              Average 0.00

55. 1 gram of ZnO, prepared from the nitrate at
280°, not ignited, gave   0.01

56. A similar experiment gave   0.02
                                                      ─────
                              Average 0.015

57. 1 gram of ZnO, prepared from zincic nitrate,
but heated to 880° in a slightly reducing at-
mosphere, gave   0.05

58. A similar experiment gave   0.15
                                                      ─────
                              Average 0.10

42. 1 gram of ZnO, prepared by gentle heating of
the nitrate at 280°, and subsequent ignition
for 30 minutes at 880° in an oxidizing atmos-
phere, gave   0.192

43. A similar experiment gave   0.192
                                                      ─────
                              Average 0.192

59. 1 gram of similar ZnO, prepared in the same
way, but heated to 670° for 3 hours and then
preserved two weeks before heating $\frac{1}{2}$ hour
at 880°, gave   0.292

60. A similar experiment gave   0.260
                                                      ─────
                              Average 0.276

61. 1 gram of more compact ZnO, prepared by
heating the nitrate rapidly, and having been
preserved for two weeks before being ignited
for $\frac{1}{2}$ hour at 880°, gave   0.387

62. A similar experiment gave   0.396
                                                      ─────
                              Average 0.392

The evidence of these results proves that the total amount
of gas retained by zincic oxide varies with every detail of the
method of preparation ; hence this amount cannot serve as a
sure guide to the temperature of ignition, unless a perfectly

uniform sample is used for all trials.[1] Of course the amounts of nitrogen found in these samples varied widely ; for the gas resulted from the decomposition of zincic nitrate, which was imprisoned in varying quantities according to the physical condition of the zincic oxide.

Since so many circumstances regulate both the amount of gas and its composition, one is not surprised that Morse and Arbuckle obtained varying mixtures with eight different preparations of zincic oxide. It is true that their expulsion of the gases continued until it had become so slow that two successive weighings with intermediate heating gave constant weight ; but the same causes of change must still have been at work, although far more slowly.

In the light of these interesting results, it seemed worth while to make a more elaborate investigation of the relation the composition of the gases held by *cupric* oxide to the temperature used in its ignition.   The material used in the following determinations was the soft powder made by the decomposition of cupric nitrate at 280°.

THE EFFECT OF TEMPERATURE OF IGNITION ON THE COMPOSITION OF GASES RETAINED BY CUPRIC OXIDE.

Time of Ignition, 1 Hour.

	Per cent. oxygen.
63. 0 32 cc. gas from 1 gram CuO heated at 520° contained	18
64. 0.34 cc. gas from 1 gram CuO heated at 520° contained	15
Average	16.5
65. 0.49 cc. gas from 1 gram CuO heated at 660° contained	6
66. 0.48 cc. gas from 1 gram CuO heated at 660° contained	5
	5.5
67. 0.47 cc. gas from 1 gram CuO heated at 750° contained	3
0.47 cc. gas from 1 gram CuO heated at 750° contained	4
Average	3.5

[1] Small quantities of such impurities as alkali and silica do not seem to affect the occlusion, however. See THIS JOURNAL, **15**, 574.

0.05 cc. gas from 1 gram CuO heated at 1000° ± contained o to 4 per cent. oxygen according to Alexander Scott.

It is evident that the cupric nitrate remaining in the cupric oxide had not been wholly decomposed by heating for an hour at 520° (experiments No. 63 and 64) and that we are dealing here with an increasing total, and a maximum similar in every respect to that already noted in the case of zinc,[1] except that in the present case more nitrogen is held, while the oxygen escapes at a much lower temperature.

THE EFFECT OF TIME ON THE COMPOSITION OF THE GAS RETAINED BY CUPRIC OXIDE.

First Series: Temperature, 500°.

(Argentic chloride easily melted; plumbic chloride scarcely melted.)

	Per cent. oxygen.
68. 0.29 cc. gas from 1 gram CuO heated 2 hours contained	25
69. 0.29 cc. gas from 1 gram CuO heated 2 hours contained	23
Average	24
70. 0.38 cc. gas from 1 gram CuO heated 8 hours contained	15
71. 0.42 cc. gas from 1 gram CuO heated 8 hours contained	14
Average	14.5
72. 0.46 cc. gas from 1 gram CuO heated 16 hours contained	8

Second Series : Temperature, 520°.

(Just below the melting-point of argentic iodide, but distinctly above that employed in the last series.)

73. 0.15 cc. gas from 1 gram CuO heated for 15 minutes contained	23
63. 0.32 cc. gas from 1 gram CuO heated for 1 hour contained	18
64. 0.34 cc. gas from 1 gram CuO heated for 1 hour contained	15

[1] See page 716.

74. 0.48 cc. gas from 1 gram CuO heated for 2
    hours contained   12
75. 0.49 cc. gas from 1 gram CuO heated for 16
    hours contained   6

Third Series. Temperature, 600°.

(Argentic iodide fused easily ; lithic chloride fused
                    slowly.)

76. 0.43 cc. gas from 1 gram CuO heated for 10
    minutes contained   12
77. 0.38 cc. gas from 1 gram CuO heated for 10
    minutes contained   12
                                                 ──
                                    Average   12
78. 0.46 cc. gas from 1 gram CuO heated for 20
    minutes contained   13

79. 0.53 cc. gas from 1 gram CuO heated for 35
    minutes contained   10
80. 0.51 cc. gas from 1 gram CuO heated for 35
    minutes contained   8
                                                 ──
                                    Average   9

Fourth Series : Temperature, 640°.

(Thallous sulphate just fused ; strontic nitrate remained
                    solid).

81. 0.21 cc. gas from 1 gram CuO heated for 2 min-
    utes contained   35
82. 0.19 cc. gas from 1 gram CuO heated for 2 min-
    utes contained   36
                                                 ──
                                    Average   35.5
83. 0.43 cc. gas from 1 gram CuO heated for 10
    minutes contained   19
84. 0.45 cc. gas from 1 gram CuO heated for 10
    minutes contained   16
                                                 ──
                                    Average   17.5
85. 0.46 cc. gas from 1 gram CuO heated for 8 hours
    contained   6
86. 0.45 cc. gas from 1 gram CuO heated for 8 hours
    contained   4
                                                 ──
                                    Average   5

It is clear that we are dealing here with a phenomenon precisely similar to that observed in the case of zinc. The decomposition of the remaining traces of nitric anhydride takes place much more slowly at low temperatures than at high ones, and the oxygen formed by this decomposition is liberated far more rapidly during the hotter ignitions.

A single series of experiments,[1] made some years ago with magnesic oxide, showed that this substance too acted in the same way, and it is probable that all the other oxides retaining traces of occluded gases would give similar results. The data obtained from magnesic oxide are repeated below, in order that all the facts may be at hand for the following consideration of the causes of the anomaly.

GAS EVOLVED FROM MAGNESIC OXIDE.

(*Temperature of Ignition was about* 700°–800°.)

1 gram MgO after ignition 30 minutes gave 3.60 cc. nitrogen and 7.2 cc. oxygen.

1 gram MgO after ignition 60 minutes gave 4.72 cc. nitrogen and 6.3 cc. oxygen.

1 gram MgO after ignition 75 minutes gave 4.84 cc. nitrogen and 4.4 cc. oxygen.

1 gram MgO after ignition 135 minutes gave 5.44 cc. nitrogen and 3.6 cc. oxygen.

1 gram MgO after ignition 195 minutes gave 5.24 cc. nitrogen and 2.8 cc. oxygen.

HYPOTHETICAL EXPLANATION.

The facts are now perfectly clear, and it remains only to account for them by means of a plausible theory. In the first place there can be no question that the gases proceed from a residue of basic nitrate imprisoned in the oxides in question ; the fact that oxides prepared from the carbonates contain little or no gas would alone be sufficient support for this point of view. The first matter to be considered is, then, the dissociation of this residual nitrate, which is probably wholly analogous to that of calcic carbonate as studied by Le Chatelier.[2] We may express this reaction, perhaps, in the follow-

[1] This JOURNAL, **15,** 576.
[2] Compt. rend., **102,** 1243 (1886). Nernst : Theor. Chem., p. 377 (1894).

ing fashion, which indicates that the proceeding is supposed to take place in the gaseous phase, while the solids enter into the reaction solely by their vapor-tension :

$$Cu(NO_3)_2.3CuO \rightleftarrows 4CuO + [N_2O_5]$$
$$\text{Vapor.} \qquad\qquad \text{Vapor.}$$
$$\downarrow\uparrow \qquad\qquad\qquad \downarrow\uparrow$$
$$Cu(NO_3)_2.3CuO \qquad 4CuO$$
$$\text{Solid.} \qquad\qquad \text{Solid.}$$
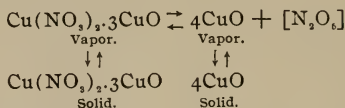
It is probable that Graham's basic cupric nitrate $Cu(NO_3)_2.$-$3Cu(OH)_2$ is dehydrated before the nitric acid begins to leave ; if it is not, of course three molecules of water must be added to the products above.[1] The gaseous products of this reaction attain the atmospheric pressure at about 280°.

The reaction represented above is evidently only a preliminary stage of the whole change ; it may have scarcely begun, or may have run almost to an end in some cases before the dissociation of the nitric anhydride begins to enter into the problem. This dissociation may be complete, resulting in a mixture of the elementary gases, or it may (and does at ordinary pressures) stop at one of the lower oxides of nitrogen. Since the gases, whatever they may be, are necessarily held in microscopic cells, while their own volume under ordinary pressure is several times that of the total volume of the solid containing them, it is obvious that the pressure under which they exist must be very great. At this great pressure the stability of N_2O_5 must be very considerably increased, for the reaction $2N_2O_5 = 2N_2 + 5O_2$ is one which pressure must seriously affect because of the change of volume concerned in it ; but more probably the peroxide of nitrogen is the first product of the reaction. In any event, it is evident that the complete separation of the oxygen and nitrogen does not take place immediately, for much less nitrogen was yielded by the specimens of each oxide heated for a short time at comparatively low temperatures than by like specimens heated longer or hotter.

[1] This conclusion is based upon the fact that no water is to be found after the ignition is completed (Proc. Am. Acad., **26**, 278). The presence of water would not affect the general tendency of the logic concerning the escape of the oxygen and nitrogen ; if, however, it actually remains until the nitrogen compounds have been split up, we must explain its final escape by a double-acting process similar to that used to explain the escape of the oxygen.

Both of these reactions, the decomposition of the cupric nitrate as well as that of the oxides of nitrogen, evidently then require time for their completion, so that the maximum of gas contents is not immediately attained. Besides being accelerated by heat they are also possibly both hastened by the escape of a portion of the oxygen, an interesting phenomenon which occurs side by side with the decomposition. To make the matter clearer, let us represent the dissociation of the oxide of nitrogen by the general formula

$$2NO_x = N_2 + xO_2.$$
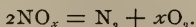
The speed of this reaction is represented by the equation

$$- \frac{dc}{d(time)} = kc^2 - k^1 c_1 c_2{}^x,$$

an expression which increases in magnitude as c_2 (the concentration of the oxygen) diminishes. Since it is probable that k^1 is very small,—that the chief tendency of the reaction is from left to right,—this cause of acceleration is not an important one. In a similar way the decomposition of the oxides of nitrogen likewise accelerates the more complex reaction into which the solids enter.

In every case this decomposition of the oxides of nitrogen, and therefore that of the cupric nitrate, had nearly advanced to completion before the oxygen had all been expelled. This led to the existence of a maximum of gas volume after a brief heating, a maximum less marked in the case of cupric oxide than in the other cases because the extra oxygen escapes from cupric oxide almost as fast as it is formed. Thus many of the apparent eccentricities in the behavior of the gases find a simple and adequate explanation. The numerous results with different oxides were sought in the hope that the relations might be capable of quantitative proof according to the law of mass action, as well as of qualitative demonstration, but the great number of possible compounds and reactions made this hope vain.

It remains only to devise an hypothesis to explain perhaps the most interesting phenomenon under discussion, to show why the oxygen is capable of escaping more rapidly than the nitrogen. Obviously diffusion or transpiration cannot account

for this; for any orifice, no matter how small, which would allow the oxygen to escape, must also allow the nitrogen to escape. The only possible explanation is the supposition that the oxygen finds its way out chemically, by uniting with metal or a lower oxide which has momentarily released some of its proper supply of oxygen. The displaced gas, being forced to find another berth, presently in its turn occupies the place of still another portion, and so on, until most or all of the excess has found its way out of prison. Of course the nitrogen cannot use this means of escape, for it is not surrounded by a compound which yields it upon dissociation; the nitrogen can only escape through holes originally present or formed by the rearrangement of the substance of the solid.

This hypothesis suggests Grotthus's obsolete explanation of electrolysis, or rather that of Clausius; for the most plausible conception is that in the hot rapidly vibrating solid a portion of the oxygen which ought to be combined with the metal is always in a free state, and that this condition, by a recurring process of dissociation and association, permits relieving the high pressure of the oxygen in the cell. It is possible that water occluded in the oxide may play the part of a go-between, but there is no experimental evidence of this.[1] It is no new idea to explain the diffusion of hydrogen through palladium, or of carbon through iron in the cementation process and other similar phenomena, by a similar mechanical conception.

Quite in accord with this point of view are a number of facts. In the first place cupric oxide, the most easily reducible of the oxides investigated, parts with its occluded oxygen with the greatest ease, at the same time obstinately retaining the nitrogen. The progressive increase in the tendency to retain oxygen in the cases of zinc and magnesium corresponds to the increase in the difficulty of reducing these oxides. In other words, the least stable oxide is the one which has the feeblest hold upon the occluded oxygen. Cupric oxide begins to lose this impurity with great rapidity at 520°, zincic oxide loses it less rapidly even at 750°, and magnesic oxide is still more obstinate. It is probable, more-

[1] See foot note on p. 722.

over, that in the cases of zinc and magnesium there is a slight amount of transpiration, for a small part of the nitrogen was found to leave at the higher temperatures. This transpiration ought to assist the oxygen also to escape, although in some-what less measure than the nitrogen ; but in spite of this pos-sibility of more rapid escape, the oxygen is still held more firmly than in the case of cupric oxide. In this latter sub-stance all the *nitrogen* is retained indefinitely at temperatures below 850°, forming the constant gas residue noted in the first experiments; only when the definite structure of the oxide is broken up, and the dissociation tension of the cupric oxide becomes so great that cuprous oxide begins to be formed, does the nitrogen take its flight. On the other hand a reducing atmosphere is needed to force zincic oxide to relinquish all its gas, unless an excessively high temperature is employed. Forty-three years ago Sainte-Claire Deville and Rivot showed that at a red heat such an equilibrium exists between zincic oxide, zinc, hydrogen, and water as to enable zinc oxide to be sublimed in a current of hydrogen, the dissociated oxide reforming when cooled.[1] This reaction undoubtedly enables the occluded gas to escape by destroying the structure of the solid when gases from the flame are present. (Experiments 57 and 58.)

Again, the fact that many solids, the oxides in question among them, manifest upon heating the peculiar contraction called '' sintering,'' is evidence of the existence of molecular instability and possibility of rearrangement. The hypothesis of partial dissociation at high temperatures is adequate to explain this.

It is obvious that the oxide, if it is really dissociated, should be capable of conducting electricity, because of the presence of traces of metal. In order to test this point, small platinum electrodes of 0.25 square centimeter in area and separated from one another by about 0.5 cm., were packed in pure specimens of the several oxides. Each porcelain cruci-ble containing an oxide was gradually heated, after having placed the two electrodes in a circuit with a delicate ampere-meter and four accumulators. When cold, the resistence of

[1] Ann. chim. phys. (3), **43**, 7, 476..

each of the oxides was at least 200,000 ohms. Upon heating, the cupric oxide began sensibly to conduct below a red heat, and at about 650° offered only about as much hindrance to the current as was afforded by 550 ohms, remaining constant at that point. On the other hand, zincic oxide fell in resistance only to about 15,000 ohms at 650°, and required fully 900° to bring it as low as 1,000 ohms; while the highest heat of the blast-lamp could not cause the magnesic oxide to transmit as much as the twentieth of a milliampere, the least current capable of being observed upon the amperemeter. It is needless to say that any possibility of the presence of a reducing atmosphere was excluded, and the fact that each oxide returned almost if not quite to its non-conducting state after cooling, is sufficient proof that the heat alone was the cause of the phenomena observed. These interesting results are fully in accord with the hypothesis that cupric oxide is slightly dissociated at a red heat, that zincic oxide is less dissociated, and that magnesic oxide, retaining its occluded oxygen with great obstinacy, is scarcely dissociated at all. Magnesic oxide, being one of the stablest of all compounds at high temperatures, could not be expected to show any appreciable dissociation or conductivity; and the wonder is, that the occluded gas is able to escape even as fast as it does.

This assumed partial thermal dissociation of solids must not be confounded with electrolytic dissociation (ionization); for the energy which determines the separation of the components in the present case is heat, and not electricity. The conductivity is not electrolytic conductivity, but only the metallic conductivity of the metal set free by a purely thermal dissociation. In order to prove this, a current of twenty milliamperes was transmitted through cupric oxide for three hours. This quantity of electricity would have carried nearly seventy milligrams of copper from a cupric solution, and since neither copper nor an oxide appeared adhering to the platinum negative electrode, it is safe to infer that the conductivity is not electrolytic. While these oxides thus conduct electricity without transference of material, it is undoubtedly true that many substances, even glass, for example, which are non-conductors when cold, become capable of carrying a cur-

rent *electrolytically* when heated. Melted salts are well known to be good electrolytic conductors, and Graetz[1] has found that this conductivity begins before the salts have melted. Our knowledge of the rationale of these facts is altogether too incomplete to afford a satisfactory explanation of all the phenomena attending the passage of electricity through solids, liquids, or gases at high temperatures; and it is perhaps unsafe to record the conductivity of cupric oxide as a definite indication of the temporary presence of metallic copper in the case under discussion.

Following is a more certain proof that this dissociation is to be considered as analogous to the decomposition of limestone by heat. Here, as there, the gas, in the present case oxygen, must have a definite pressure of dissociation; but no appreciable amount of metal or lower oxide can form when the tension of the oxygen in the surrounding atmosphere is greater than this definite pressure. On the other hand, cupric oxide should not lose only its occluded oxygen, but all the oxygen that normally belongs to it, leaving metallic copper (or at least cuprous oxide), when heated in a perfect vacuum or in an inert atmosphere, if the hypothesis under consideration is tenable. This decomposition begins even in the air at about 1,000°. The search in chemical literature revealed a statement by Hilditch that cupric oxide ignited at lower temperatures in a vacuum weighs less than it did before, as well as one by Morley, that the same substance slowly evolves a gas when heated in a vacuum.[2] Since it is hard to tell whether this evolution might not be merely that of the occluded gases, it was thought worth while to repeat the experiment.

Two grams of cupric oxide, which had been ignited for a long time in pure air until constant in weight, were found to evolve a gas steadily when heated in a vacuum to about the melting-point of common salt (790°), provided that the gas was removed by a Sprengel pump as fast as it was formed. When allowed to attain equilibrium, this gas (which repeated analysis showed to be almost pure oxygen containing only traces of

[1] Wied. Ann., **40**, 18 (1890).

[2] Hilditch : Chem. News, **49**, 37 (1884). Morley : Am. J. Sci., **41**, 231 (1891).

nitrogen and carbon dioxide) was found to possess a tension of two or three-tenths of a millimeter of mercury. A portion of the same material was heated for many hours more in a crucible to a full red heat; but upon subsequently heating it in a vacuum the evolution of gas proceeded just as before. Since all the occluded oxygen except two or three per cent. had been expelled by the preliminary heating, this must have been structural oxygen. The conclusion was confirmed by the discovery of red cuprous oxide in the residue. Repetitions of the experiment showed that the tension of the gas increased enormously with the temperature, exceeding a millimeter before the glass became so soft as to collapse. In some of the experiments the best Bohemian glass was used, in others the hardest made in Jena. The nature of the glass seemed to be without influence on the result. The amount of gas evolved in a given time naturally depends upon the efficiency of the pump, as well as upon the temperature; in one of the experiments two cc. of oxygen were obtained in eight hours.

Ignition of the substance in an inert atmosphere should produce the same effect. Since cupric oxide is slightly dissociated by heat, perceptible amounts of oxygen should be removed by heating it in nitrogen, just as carbonic acid is removed from limestone by heating it in a current of air. This dissociation of cupric oxide must have its effect on any process involving the ignition of cupric oxide in a vacuum or in an inert gas. The determination of organic nitrogen by means of the Sprengel pump, for example, must be affected by it. The use of carbon dioxide as a displacing medium in the Dumas method, probably disposes of the error, however; for carbon dioxide is itself dissociated by heat, and it undoubtedly furnishes enough oxygen to diminish greatly the decomposition of the cupric oxide.

In the light of these results, it is obviously advisable, when one desires to remove oxygen from a mixture of gases by means of hot copper, to maintain the last portion of the tube at a comparatively low temperature. Even then the issuing gas may not be absolutely free from oxygen.

Every one knows that auric oxide is excessively unstable,

and that argentic oxide is completely decomposed even in an atmosphere of pure oxygen at comparatively low temperatures. The present results merely extend this behavior, in a much smaller degree, to cupric oxide, and the hypothesis carries the idea still further. The dissociation of zincic oxide must of course be yet less, while the tension of oxygen above magnesic oxide even at high temperatures must be an infinitesimal far less in value than the tension of the gas in the vacuum needed for the production of X-rays.

According to the phase rule and the law of mass action these reactions must take place in the gaseous phase,—the only one present of variable composition. As an example, the case of copper is given below :—

$$4\ CuO \leftrightarrows 2\ Cu_2O + O_2$$

Vapor.	Vapor.	Gas.
↑↓	↑↓	
$4\ CuO$	$2\ Cu_2O$	
Solid.	Solid.	
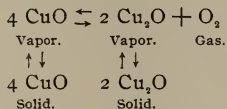
The occluded oxygen is supposed to escape by the oscillation, backward and forward, of this heterogeneous reaction. The ability of the system to be first dissociated and then associated in another place where more oxygen is present presupposes, however, great internal activity in the substance of the hot solids : and this internal activity is the most interesting conclusion to be drawn from the phenomena under discussion.

In short, no matter what point of view one adopts, or what mechanical picture one forms of the reaction, the necessity of ascribing the rapid escape of the oxygen to internal rearrangement seems to be inevitable.

Morse and Arbuckle, in the course of some admirable work upon the atomic weight of cadmium which they have just completed,[1] had occasion to measure the gases occluded by cadmic oxide made from the nitrate. As one would expect, this oxide holds its occluded oxygen more firmly than copper, but less firmly than zinc. In fact, the behavior of the substance, according to Morse and Arbuckle's description, probably accords well with the hypothesis under consideration. The fact that Rogers and I found

[1] This JOURNAL, **20**, 536.

no gas in our cadmic oxide in 1892 is easily accounted for by
the circumstance that we used a bright red heat in the igni-
tion, the oxide parting with both gases by the disintegration
of its original structure as the oxide of copper did with Scott.
Since cadmium is volatile at high temperatures, however, it
was natural that its dissociated oxide should have a wider
opportunity of rearrangement than in the case of copper ; and
hence the crystalline structure of the ignited oxide observed in
1892. The volatility of cadmium explains the sublimation of
the oxide observed by Morse and Arbuckle ; this sublimation
was really a dissociation and recombination like the sublima-
tion of sal ammoniac.

Nickel, another metal whose oxide was investigated by
Rogers, probably occupies its expected place near cadmium,
as far as its oxide's capacity to retain oxygen is concerned.
In some recent experiments in this laboratory, Cushman suc-
ceeded in partially decomposing nickelous oxide in a stream
of nitrogen below 1200°. All these considerations are concor-
dant with the hypothesis devised to explain the escape of
occluded oxygen from metallic oxides.

The only point regarding this occlusion of gases left unex-
plained is the fact that in the experiments of Morse and Ar-
buckle the total amount of gas was in every case nearly the
same, although the proportion of oxygen and nitrogen varied.
This is a very interesting circumstance. The experimenters
ignited their oxide to constant weight, in other words, until
two successive ignitions caused no appreciable change ; but
it does not follow from this that the evolution of gas had
ceased,—one can only maintain that it had become so slow as
to be inappreciable. Evidently, then, the question to be
answered is,—Why has the oxygen more difficulty in esca-
ping when a small amount of nitrogen is present than when a
large amount is present? The reason of this eccentricity may
be because those specimens which contain the most gas are
naturally the most porous and loosely held together, although
usually formed in larger individual aggregations ; and the
freer atomic and molecular motion allowed by the looser
structure may permit the oxygen to leave more rapidly. Hence

in each case the sum of the oxygen and nitrogen amounted to about the same volume. This hypothesis within an hypothesis is rather too uncertain to deserve much emphasis, however.[1]

In the course of some of my old experiments on the impurities in cupric oxide, it became necessary to reduce the substance in a current of carbon monoxide. Referring to this work, Scott, in the paper already cited,[2] expresses surprise at the existence of an admixture of hydrogen in this gas. His experience agrees with that of Stas in finding only a small amount of such gaseous impurity in carbonic oxide obtained from oxalic acid, while my results indicated a large amount. Lord Rayleigh, in the course of his recent valuable work on the density of gases,[3] concludes that his carbonic oxide also was free from hydrogen or hydrocarbons; and indeed there is no reason why this result should not be easily attained if one uses pure materials. Lord Rayleigh explains the existence of hydrogen in my carbonic oxide by drawing attention to the fact that in my case the gas, dried only by calcic chloride, was passed over red hot platinum sponge.

This explanation is undoubtedly correct. Many experimenters have shown that the reaction $CO + H_2O = H_2 + CO_2$ is one easily reversible at high temperatures,[4] and in the presence of a large excess of carbon monoxide, it is obvious that nearly all of the trace of aqueous vapor would be reduced. For my purpose at the time, the source of the hydrogen was of no importance; it was only necessary to know the exact amount of the impurity, and this was suitably determined. It is satisfactory to know the cause of the discrepancy, however, as well as to know that it is easier to prepare carbon

[1] In this connection it is a matter of interest to note that Ramsay (Phil. Mag. [5] **38**, 206, (1894)) has found that the presence of nitrogen in a palladium bulb seems to prevent, to some extent, the diffusion of hydrogen into it. This observation is not unlike Morse and Arbuckle's; but if as a matter of fact an indifferent gas can produce such an effect, our present notions concerning semipermeable septa demand some revision.

[2] *Loc. cit.*, p. 563.

[3] Proc. Roy. Soc., **42**, 204, (1898).

[4] Bunsen : Ann. Chem. (Liebig), **85**, 137 (1853). Horstmann : *Ibid.*, **190**, 228 (1878). Bötsch : *Ibid.*, **210**, 207. And especially Hoitsema : Ztschr. phys. Chem., **25**, 668, as well as others.

monoxide almost free from hydrogen than seriously contaminated with it. More often than we suspect, perhaps, are our carelessly planned efforts at purification apt thus to introduce more impurity than they eliminate.

In a recent number of the Journal of the American Chemical Society (March, 1898), F. R. M. Hitchcock has published a preliminary paper upon the occlusion of various gases by the oxides of the metals, having apparently overlooked the Harvard investigations. It is satisfactory to see the phenomenon widely recognized ; for an appreciation of this serious cause of possible constant error will result in the publication of fewer erroneous determinations of atomic weights than have appeared in the past. One should also bear in mind the fact that nitric acid is not by any means the only substance which is liable to leave appreciable contamination in material from which it has been expelled by heat. The number of such occlusions is far greater than most analysts imagine ; this fact is not realized because the minute residues are often so hard to detect.

The evidence of this paper proves that in reality no discrepancy exists between the results of Scott, and Morse and Arbuckle, and those obtained at Harvard. The apparent disagreements were caused by the fact that the later experimenters investigated parts only of the wide field outlined in 1892, the relation of the parts to the whole being not wholly realized. The paper also shows that the unequal escape of oxygen and nitrogen imprisoned in the oxides of metals is a phenomenon of great interest, capable of shedding light on the internal kinetics of solids.

CAMBRIDGE, May 1, 1898.

NEW EXPERIMENTS ON THE QUANTITATIVE SYNTHESIS OF WATER.

By Edward H. Keiser.

In the complete syntheses of water made in recent years for the purpose of determining the relative atomic weights of oxygen and hydrogen, the apparatus has been so constructed that the hydrogen was burnt at a jet in an atmosphere of oxygen. When the gases are combined in this way it is found that towards the end of the experiment it is difficult to keep up the combustion, the flame gradually dies out, and finally a residual gas remains in the combustion chamber, consisting of unburnt hydrogen and oxygen and whatever impurities were present in these gases. This residual gas volume must then be pumped out, measured and subjected to eudiometric gas analysis. From the volumes of hydrogen and oxygen thus found the weights of these gases that have remained uncombined must be calculated, and these weights must be deducted from the weights of oxygen and hydrogen found by direct weighing. The final weight of each gas is, therefore, not the result of weighings with the balance, but is dependent upon the accuracy of a volumetric gas analysis involving a number of eudiometric operations and calculations.

With the hope of making a complete quantitative synthesis of water in such a way that the weights of hydrogen, oxygen, and water could be directly determined with the balance, the method described below was devised. It is based upon the fact that hydrogen when occluded in palladium is completely oxidized to water when the palladium hydride is brought in contact with an excess of oxygen.

In outline the steps of the process are as follows : First, a glass vessel with two communicating compartments, one of which is filled with phosphorus pentoxide, is exhausted with an air-pump and weighed. Second, metallic palladium is put into the second compartment, and after exhausting the weight is again determined. Third, pure hydrogen is now admitted, and after the palladium is saturated the vessel is again connected with the air-pump and a portion of the gas is pumped

out and again weighed. The difference between the second and third weighings gives the weight of hydrogen to be oxidized. Fourth, pure oxygen is now slowly admitted, water is formed, and the vessel becomes warm. By regulating the current of oxygen the temperature can be kept down so that it does not rise much above that of surrounding objects. Finally, after all the hydrogen is oxidized and the vessel is full of oxygen, the excess of oxygen is pumped out, the gas, however, in going out is made to pass through the phosphorus pentoxide, so that all water is retained. The vacuous vessel is again weighed. The difference between the third and fourth weighings gives the weight of oxygen that has united with the hydrogen. Fifth, after the palladium has stood in the vacuum over the phosphorus pentoxide and the water has

Fig. 2.

Fig. 1.

united with the pentoxide, the palladium is removed, and the vessel after exhausting is weighed. The difference between the first and fifth weighings gives the weight of water formed. This weight must agree closely with the sum of the weights of hydrogen and oxygen as previously found, if the experiment is to be regarded as trustworthy.

Fig. 1 shows the construction of the vessel that was used. It consisted of a wide glass tube $5\frac{1}{2}$ cm. in diameter, 19 cm. in length; it was drawn down and closed at the bottom by a narrow tube carrying a glass stop-cock, and at the top by a cap with a three-way stop-cock. The cap was connected with the tube by means of a ground glass joint. The wide tube was constricted as shown in the figure, so as to form two compartments. The lower one served to hold the phos-

phorus pentoxide, the upper one the palladium. The palla-

dium in the form of sponge was placed in the glass tube shown in Fig. 2. This tube was of such diameter that it could be easily placed inside of the larger tube after the cap had been removed. The constriction prevented it from touching the pentoxide. The dotted lines in Fig. 1 are intended to show the palladium tube in position.

Three tubes of the kind represented in Fig. 1 were made of the same kind of glass and of as nearly equal dimensions as possible. The volume of each was determined by hydrostatic weighing. The volumes of the smaller ones were made as nearly equal as possible to that of the larger one by adding compensating bulbs. Two of the tubes served as counterpoises to the working tube, one to counterpoise it for the first and fifth weighings, when the working tube contained no palladium, the other for the second, third, and fourth weighings, when both palladium and pentoxide were present. Lead in the form of shot was put into the counterpoise tubes until they were somewhat heavier than the working tube. In all the weighings it was, therefore, necessary to add to the scale-pan carrying the working tube but few weights, and these were of small value. The correction of the weights for air displaced was very small, and as the weights of hydrogen and oxygen were not large, the reduction of these weights to a vacuum only affected the ratio in the fourth decimal place, which was within the limits of experimental error.

A Troemner balance with aluminium beam, having a capacity of 250 grams on each scale pan, was used. The method of weighing by reversals was used in all the determinations. With the working tube and the weights on one side, the counterpoise on the other, the fractions of milligrams were found by means of the vibrations and the sensibility. Then the loads were reversed and the weight found in the same way. The mean of the values was taken as the result of one weighing. At intervals of twelve hours the weighing was repeated. If there had been any appreciable leakage of air into the tube, it would have been possible to detect it in this way. The final value for a weight was thus the result of at least two, and in some cases of three and four double weighings made at intervals of twelve hours.

A Toepler mercury air-pump, without stop-cocks, was used in making the exhaustions. Connected with the pump was a phosphorus-pentoxide ∪-tube. The pentoxide that was used in the working tube was purified by subliming the commercial oxide in a stream of dry air. To prevent the pentoxide from falling into the narrow glass tube at the bottom of the working tube, a small spiral of platinum gauze was put into the narrow tube, and a loose plug of previously ignited asbestos was placed on top of the gauze. The pentoxide filled the lower compartment to within three millimeters of the constriction, and in quantity was largely in excess of the amount required to unite with the water formed. The palladium sponge was in the form of cohering masses, obtained by the reduction of pure pallad-ammonium chloride in a stream of hydrogen. It was free from ammonium chloride. The tube
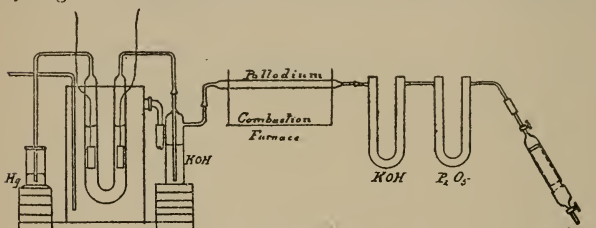
Fig. 3.

for holding the metal was open at the top, and was provided with a number of small holes near the bottom, the object of which was to facilitate the passage of the aqueous vapor from the palladium to the phosphorus pentoxide. The palladium tube when not in the working tube was kept in a desiccator over phosphorus pentoxide.

After putting the pentoxide into the working tube, exhausting and weighing it, air, dried over pentoxide, was slowly admitted. The cap was then removed and the palladium tube put into position, and the cap again instantly replaced. The tube was again exhausted and weighed. Thereupon it was charged with hydrogen. For this purpose it was connected by means of the three-way cock with an apparatus furnishing a stream of purified electrolytic hydrogen. This apparatus is shown in Fig. 3. The ∪-tube with electrodes for decom-

posing dilute sulphuric acid, is shown on the left. It was
kept cool by means of cold water flowing in the outer cylin-
der. The electrolytic hydrogen passed first through a con-
centrated solution of caustic potash, then over palladium
sponge contained in a combustion tube. The metal in the
middle of the combustion tube was kept at a dull red heat;
that at the ends was only slightly above the ordinary tem-
perature. This palladium served to remove any oxygen that
may have been present in the hydrogen. Other substances
that might have been taken up by the palladium in the work-
ing tube would also have been removed. Thereupon the gas
passed through ∪-tubes containing freshly fused caustic
potash and resublimed phosphorus pentoxide. After the cur-
rent of hydrogen had been running for about an hour and es-
caping at the three-way cock, it was slowly admitted to the
palladium. The electrolytic oxygen escaped through the
mercury shown on the extreme left. By raising or lowering
the column of mercury, the pressure in the interior of the ap-
paratus could be easily regulated.

After the palladium was saturated, the working tube was
connected with the air-pump and about a liter and a half of
gas was pumped out. Gas not taken up by the palladium
was thus removed. After weighing, the tube was again at-
tached to the electrolytic apparatus, which now, with reversed
current, was furnishing a stream of pure dry oxygen. The
oxygen was also passed over hot palladium to remove hydro-
gen and any other substances that might possibly be
present and capable of uniting with the metal. The oxygen
was dried with fused caustic potash and phosphorus pentox-
ide. After the oxygen had been flowing through the appa-
ratus for about an hour and escaping at the three-way cock,
the latter was cautiously opened so as to admit a very slow
stream of gas. Moisture was at once deposited on the walls
of the tube. If at this point a rapid stream of oxygen be ad-
mitted, the palladium at its upper surface can be seen to
glow. This, however, was avoided in all the quantitative
experiments recorded below. By admitting the oxygen
slowly, the temperature of the working tube was not allowed
to rise much above that of the surrounding air. From four to

five hours were required to oxidize the hydrogen. Finally when the tube was full of oxygen, it was allowed to stand over night. During this time most of the water combined with the pentoxide. Then the lower stop-cock was connected with the pump and the excess of oxygen withdrawn. This excess of oxygen in passing out went through the pentoxide, so that no moisture was removed from the tube in this way. The exhausted tube was weighed, and, after the palladium had been standing over the pentoxide in the vacuum for at least forty-eight hours, dry air was admitted, the palladium removed, and after again exhausting the tube was weighed. This last weighing, taken in connection with the first, gave directly the amount of water taken up by the pentoxide.

To give an idea of the details of calculation, the complete data of the second experiment are here given.

1st weighing. Tube + P_2O_6 + weights against tare No. 1.	2nd weighing. Tube + P_2O_6 + Pd + weights against tare No. 2.	3rd weighing. Tube + P_2O_6 + PdH + weights against tare No. 2.	4th weighing. Tube + P_2O_6 + Pd + H + O + weights against tare No. 2.	5th weighing. Tube + P_2O_6 + H_2O + weights against tare No. 1.
3.92084	3.67523	3.39591	1.17682	1.42185
3.92124	3.67538	3.39598	1.17714	1.42178
3.92104	3.67530	3.39594	1.17698	1.42181

Weight of hydrogen = 3.67530 — 3.39594 = 0.27936
"   " oxygen   = 3.39594 — 1.17698 = 2.21896

"   " hydrogen + oxygen =   2.49832
"   " water = 3.92104 — 1.42181 =   2.49923

Difference   0.00091

Ratio of hydrogen to oxygen = 0.27936 : 2.21896 = 1 : 7.943
"   "   "   " water = 0.27936 : 2.49923 = 1 : 8.946

Reducing the weights to a vacuum has no appreciable effect upon the ratio. Thus reduced weight of hydrogen = 0.27936 + 0.00002 = 0.27938. Reduced weight of oxygen = 2.21896 + 0.00030 = 2.21926. Ratio H : O = 1 : 7.943. Reduced weight of water = 2.49923 + 0.00032 = 2.49955. Ratio of H : H_2O = 1 : 8.946.

Altogether six determinations were attempted, two of these gave results that showed that there was either leakage or imperfect drying of the gases, because the direct weight of water in one of these exceeded the sum of the weights of hydrogen and oxygen by 6 milligrams, and in the other case by 4.5 milligrams. These have accordingly been rejected. The results obtained from the others are as follows :

No.	Wt. of H.	Wt. of O.	Sum of H + O.	Wt. of H$_2$O found.	Difference.
1	0.27549	2.18249	2.45798	2.45975	0.00177
2	0.27936	2.21896	2.49832	2.49923	0.00091
3	0.27091	2.15077	2.42168	2.42355	0.00187
4	0.26845	2.13270	2.40115	2.40269	0.00154

Calculating the ratio of oxygen to one part of hydrogen from the second and third columns, we have :

No.	Ratio.
1	7.922
2	7.943
3	7.939
4	7.944
Mean	7.937

If the weights are reduced to a vacuum, the ratios become :

No.	Ratio.
1	7.923
2	7.943
3	7.940
4	7.945
Mean	7.937+

From the second and fifth columns we obtain the ratio of water to one part of hydrogen.

No.	Ratio.
1	8.929
2	8.946
3	8.946
4	8.950
Mean	8.943

The first ratio gives, for the atomic weight of oxygen, the number 15.874, the last one 15.886. The mean of the two is 15.880.

ON THE METAPHOSPHIMIC ACIDS (III).[1]

By H. N. STOKES.

In the preceding papers on the metaphosphimic acids[2] it was shown that the two then known phosphonitrilic chlorides, $P_3N_3Cl_6$ and $P_4N_4Cl_8$, give, on saponification, two well-defined acids, trimetaphosphimic acid, $P_3N_3O_6H_6$ and tetrametaphosphimic acid, $P_4N_4O_8H_8$. In a later investigation[3] the existence of the higher phosphonitrilic chlorides $P_5N_5Cl_{10}$, $P_6N_6Cl_{12}$, and $P_7N_7Cl_{14}$ was shown, and it was further demonstrated that the series does not end here, but is continued through a number of members, which are incapable of separation by existing methods, and terminates with a remarkable rubber-like polymer of high molecular weight.

The work outlined in the present paper was begun with the expectation of finding that each of the new phosphonitrilic chlorides would give, on saponification, the corresponding metaphosphimic acid of the general formula $(PNO_2H_2)_n$. The result, however, has not justified this anticipation. It has been found that penta- and hexaphosphonitrilic chlorides give true penta- and hexametaphosphimic acids, $(PNO_2H_2)_5$ and $(PNO_2H_2)_6$, but that heptaphosphonitrilic chloride gives, not $(PNO_2H_2)_7$, but an acid $(PNO_2H_2)_7 + H_2O$. The metaphosphimic series, therefore, appears to be limited by the acid $(PNO_2H_2)_6$.

The metaphosphimic acids are the lactams of the imidophosphoric amides,[4] and it is therefore not surprising that there should be a certain similarity of behavior between these and certain organic oxy- and amido-acids. The γ- and δ-oxy- and amido-acids, while existing as salts in alkaline solution, pass more or less readily in the free state into the inner anhydrides, the lactones and lactams, a behavior which is not observed when the hydroxyl or amido-group is still further removed from the carboxyl. Joh. Wislicenus has shown[5]

[4] The imidophosphoric acids consist of chains of alternate NH and PO groups, the first being imidodiphosphoric acid, $PO(OH)_2.NH.PO(OH)_2$. This, and diimidotriphosphoric acid are described in the paper on trimetaphosphimic acid, and triimidotetraphosphoric acid in the present paper. The amides, of which the metaphosphimic acids are the lactams, may be regarded as imidophosphoric acids having one terminal hydroxyl replaced by an amido group.

[5] Räumliche Anordnung der Atome, S. 67.

that the geometric configuration of the lactone-giving acids is such as to bring the reacting groups into close proximity, thus admitting of inner anhydride formation, while in other cases this is not possible, owing to their remoteness. Von Baeyer,[1] in his well-known "tension theory," has shown that the series of methylene-ring hydrocarbons, $(CH_2)_n$, may be expected to possess a maximum of stability in the pentamethylene ring, a ring in which there is the least "strain," because the attraction of the carbon atoms for each other acts very nearly in the direction which the valences naturally assume, a deduction which has been confirmed by recent work on the reduction of aromatic hydrocarbons, showing the tendency of these to form pentamethylene rings when reduced.[2]

The speculations of Wislicenus and Von Baeyer admit of application to the series of acids derived from the phosphonitrilic chlorides, and as far as the subject has been worked out, the analogy is a complete one. The acids in the open form are amides of imidophosphoric acids; those with from three to six phosphorus atoms have the open form in alkaline solution, from which they are thrown out by silver nitrate as salts of the general formula $(PNO_2Ag_2) + H_2O$, but in acid solution they spontaneously form the inner anhydrides; *i. e.*, the metaphosphimic acids, which can be precipitated as silver salts of the general formula $(PNO_2HAg)_n$. The acid with seven phosphorus atoms, on the contrary, does not form the anhydride under any conditions. Not only does the series possess an extremely marked maximum of stability in tetrametaphosphimic acid, but the higher acids, on being subjected to energetic attack, break up, yielding this body.

In my former paper, I have assumed that tri- and tetrametaphosphimic acids contain phosphorus-nitrogen rings:
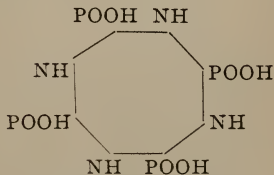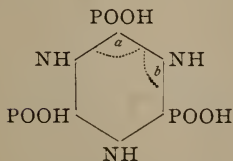
[1] Ber. d. chem. Ges., **18**, 2277. [2] Zelinsky : Ber. d. chem. Ges., **30**, 387, 1539.

We know nothing of the steric relations of phosphorus and but little of those of nitrogen, and have therefore no definite theoretical grounds for assuming the magnitude of the angle a formed by the lines joining a POOH group with two NH groups, nor of the angle b formed by lines connecting a NH group with two POOH groups, in the case when these are free to assume a relation of greatest stability or least tension, as in an open chain. Neither can we assert that in a six-sided ring, P_3N_3, with alternate phosphorus and nitrogen, the angles a and b must each be 120°. We are, however, justified in assuming that the *mean* of a and b is 120°. Similarly in an eight-sided ring, P_4N_4, the *mean* angle is 135°, even though a may be 180° and b 90°.

Experiment having shown that tetrametaphosphimic acid, $P_4N_4O_8H_8$, is vastly more stable than any other acid of the series, we may regard the angle $\dfrac{a+b}{2}$ of the octagonal nucleus P_4N_4, which is 135°, as that which most nearly coincides with the angle of least tension in the sense of Von Baeyer's theory, and as approximating to that which would be assumed in an open chain, and we may expect that the stability of each ring will be less the more the angle $\dfrac{a+b}{2}$ differs from 135°. In the following table the mean angle and its difference from 135° are shown :

Ring.	Number of sides.	Mean angle.	Difference from 135°.
PN	2	0°	−135°
P_2N_2	4	90°	− 45°
P_3N_3	6	120°	− 15°
P_4N_4	8	135°	0°
P_5N_5	10	144°	+ 9°
P_6N_6	12	150°	+ 15°
P_7N_7	14	154.3°	+ 19.3°
P_8N_8	16	157.5°	+ 22.5°

It is therefore to be expected that as we ascend in the series there will be a very rapid increase of stability to a maximum, followed by a gradual decrease. This coincides with what we find. $P_3N_3O_6H_6$ is vastly less stable than $P_4N_4O_8H_8$; the latter may be heated for hours with acids

without complete decomposition, while the former is destroyed under the same conditions in a few minutes.[1] $P_5N_5O_{10}H_{10}$ is much less stable than $P_4N_4O_8H_8$, but markedly more stable than $P_3N_3O_6H_6$, corresponding to the difference of only 9° from 135° in one case against 15° in the other. $P_6N_6O_{12}H_{12}$ is perceptibly less stable than $P_5N_5O_{10}H_{10}$ and finally the ring P_7N_7 of heptametaphosphimic acid is incapable of existence under the usual conditions, and as a result we get, instead of the ring acid $P_7N_7O_{14}H_{14}$, the open chain $P_7N_7O_{15}H_{16}$.

When any of the acids above tetrametaphosphimic acid is broken up, the latter is formed in considerable amount. This may be explained in two ways : either the P_4N_4 nucleus exists as such in the higher acid, or it is formed from the decomposition products. The former is highly improbable, for, considering its great stability, it should persist and be found in nearly theoretical amount, which is by no means the case. ($P_5N_5O_{10}H_{10}$ gave 12 per cent. and $P_6N_6O_{12}H_{12}$ 30 per cent. of the theoretical.) Its formation from the decomposition products is easily explained on the tension hypothesis. If a ring of POOH and NH groups be broken up by the action of a stronger acid, the molecules resulting from its decomposition will tend to assume a configuration determined by the mean angle of least tension, 135°, and this configuration in the case of the molecule of triimidotetraphosphoric amide will be either a zigzag line or the form represented by
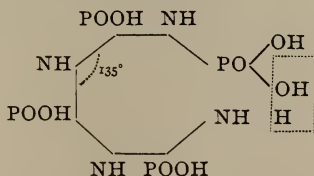
a configuration which admits of the formation of the anhydride or lactam, which is nothing else than tetrametaphosphimic acid. A theoretical yield of this cannot be expected, for when a chain, P_8N_8, for example, is further broken up, the disruption may occur at any one of nine points, but only

[1] This JOURNAL, **18**, 653, 785.

when one of the resulting products contains P_4N_4 can tetra-metaphosphimic acid be formed. A simple calculation shows that at most only 27 per cent. of that required by the equation

$$P_5N_5O_{10}H_{10} + 2H_2O = P_4N_4O_8H_8 + NH_4H_2PO_4$$
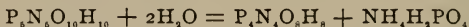
can be expected. A chain P_5N_5, however, offers more chances for the formation of fragments containing P_4N_4 and hence, as actually found, the yield of tetrametaphosphimic acid is greater, instead of less, as would be the case if the nucleus of this acid existed as such in hexametaphosphimic acid.

The first two chloronitrides, $PNCl_2$ and $P_2N_2Cl_4$, have not been obtained, and of the corresponding mono- and dimeta-phosphimic acids the former is unknown and the existence of the latter questionable. Mente[1] has described salts of an acid to which he gives the formula of dimetaphosphimic acid, $P_2N_2O_4H_4$, but no proof is given that it is not some other poly-mer of PNO_2H_2, and the method by which he obtained it is one which is not likely to give a body of this molecular weight. The dimetaphosphimic ring would have a mean angle of 90°, which differs from that of tetrametaphosphimic acid by 45°. Such a ring should be much less stable than even that of heptametaphosphimic acid, and it is therefore quite possible that it is incapable of existence as such, and can exist only as the hydrate $P_2N_2O_6H_6$. This is perhaps the acid described by Gladstone[2] as pyrophosphodiamic acid.

The chloronitride series presents a maximum of stability in triphosphonitrilic chloride, but this is by no means as marked as that existing in the acid series. That such a maximum should occur in one case in a ring of six sides, and in the other in an eight-sided ring, and that the series should be limited in one case and unlimited in the other, involves no contradiction. Triphosphonitrilic chloride is stable only in the sense that it is formed in the largest amount and that its chlorine is most tenaciously held, while the term is applied to the acids as indicating the difficulty with which the ring is broken open. In the one case, the series consists of polymers of $—PCl_2=N—$ and in the other of $—POOH—NH—$, and

[1] Ann. Chem. (Liebig), **248**, 244.

[2] Q. J. Chem. Soc., **3**, 135, 354; Ann. Chem. (Liebig), **76**, 79; **77**, 315; J. Chem. Soc. [2], **2**, 231.

the two series cannot therefore be considered analogous in a stereochemical sense.

Only tri- and tetrametaphosphimic acids give characteristic salts. The salts of the acids with 5, 6, and 7 atoms of phosphorus are totally devoid of crystallizing power, the alkaline salts being precipitated from aqueous solution by alcohol as syrups, which can easily be converted into the solid form by dehydration with absolute alcohol, but which are still wholly amorphous. The tendency to diminished acidity of unneutralized hydroxyls, well known in the case of orthophosphoric acid, is here apparent, and to an increasing extent as we rise in the series. Trimetaphosphimic acid forms a salt with 3 atoms of sodium which has neutral reaction and is not decomposed by strong acetic acid ; tetrametaphosphimic acid readily gives salts with 2 and 4 atoms of sodium. The five-atom sodium salt of pentametaphosphimic acid is strongly alkaline and shows a tendency to hydrolytic dissociation, and the same tendency is still more marked in the higher acids. Owing to this, and to their amorphous nature, it is impossible to obtain salts of definite composition from any but the first two acids, unless certain conditions are rigidly adhered to. Qualitative differences between the analogous salts of the higher acids are almost wanting, and only a quantitative study, and a knowledge of their derivation serve to distinguish them. As with other phosphorus-nitrogen acids, no ammonia is evolved on boiling with alkalies.

Amides of the Metaphosphimic Acids.

Gerhardt[1] has described, under the name "phosphamide," a body of the empirical composition PN_2OH_4, which he obtained by action of ammonia and water on phosphorus pentachloride, and to which he gave the formula $PO \begin{array}{l} \diagup NH \\ \diagdown NH_2 \end{array}$. This corresponds to the amide of a metaphosphimic acid, but its properties indicate that it is probably a substance of high molecular weight. I have attempted to obtain amides of the first three metaphosphimic acids by acting on the corresponding chloronitrides with gaseous or strong aqueous ammonia. The ef-

[1] *Ann. chim. phys.* [3], **18**, 188.

forts were but partially successful. The P : N ratio is sometimes rather higher, sometimes rather lower, than is required by the formula $(PN_4OH_5)_n$. They have none of the properties of Gerhardt's phosphamide, but are extremely soluble in water, uncrystallizable and unstable, and have weakly acid properties, forming alkali and silver salts, which, however, are of very variable composition and of ill-defined properties. Like the metaphosphimic acids, they give off no ammonia on boiling with alkali, but are easily decomposed on treatment with acids.

General Summary.

The principal results of the preceding investigations may be summed up as follows :

1. There exists a series of bodies of the general formula $(PNCl_2)_n$, beginning with Liebig's chloronitride of phosphorus, and extending indefinitely upward.

2. Each of these bodies yields, on saponification, an acid with the same number of phosphorus and nitrogen atoms.

3. The first four of these acids exist in two forms : the lactam form, $(PNO_2H_2)_n$, (metaphosphimic acids), where n is either 3, 4, 5, or 6, which is formed only in neutral or acid solution, and the open chain form $(PNO_2H_2)_n + H_2O$, formed under the influence of alkalies.

4. The acid derived from the fifth chloronitride, $P_5N_5Cl_{10}$, and possibly those from the higher members, do not form lactams, but persist in the open form under all circumstances.

5. The properties of these acids, with respect to stability, power of forming lactams, and nature of decomposition products, may be explained by stereochemical considerations, analogous to those of Von Baeyer on the methylene hydrocarbons and of Joh. Wislicenus on the lactones.

EXPERIMENTAL PART.

Saponification of the Phosphonitrilic Chlorides.—As pointed out in the preceding papers, triphosphonitrilic chloride is conveniently saponified by shaking its ethereal solution with an aqueous solution of sodium acetate, and tetraphosphonitrilic chloride in a similar manner with water, the trifling quanti-

ties of secondary decomposition products being easily re-
moved. These methods cannot be applied to the higher chlo-
rides, for the secondary products formed by the liberated acetic
or hydrochloric acid cannot be separated from the main
product owing to the uncrystallizable nature of the latter. A
smooth saponification without secondary products may be ef-
fected by using sodium hydroxide in sufficient amount to keep
the solution always strongly alkaline.

4 parts chloride are dissolved in about 20 parts alcohol-free
ether and shaken with a solution of 5 parts pure sodium
hydroxide in 20 parts water. A bottle with a carefully paraf-
fined glass stopper must be used, corks being inadmissible as
they give rise to colored products which cannot be removed.
The shaking is conveniently effected by a rotator, moved by
a small electric motor, and about fifty hours are sufficient for
complete saponification. As soon as the ether is found to be
practically free from chloronitrides, the alkaline solution is
drawn off and precipitated by 2 or 3 volumes of alcohol.
This throws down the sodium salt as a thick syrup, which is
repeatedly washed by stirring with 60 per cent. alcohol, dis-
solved in water, reprecipitated by alcohol and again washed
in the same way until it is free from sodium chloride. It is
then dehydrated by stirring, kneading, and finally pulveri-
zing under renewed portions of absolute alcohol. After stand-
ing several hours under absolute alcohol it is filtered off and
dried *in vacuo* over sulphuric acid. The yield in each case is
about 90 per cent. of the theoretical, the remainder being lost
in the alcoholic solution.

<div style="text-align:center">

Pentametaphosphimic Acid,

$$POOH \underset{NH.POOH.NH.POOH}{\overset{NH.POOH.NH.POOH}{<}} >NH.$$

</div>
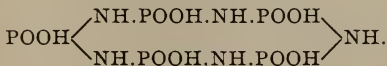
This is the lactam of *amidotetraimidopentaphosphoric acid*,

<div style="text-align:center">

$$POOH \underset{NH.POOH.NH.PO(OH)_2}{\overset{NH.POOH.NH.PO}{<}} \overset{OH}{\underset{NH_2}{<}}.$$

</div>
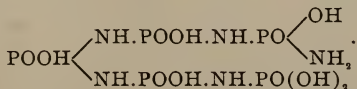
It exists in the lactam form in the five-atom silver salt and

apparently in the solution of its acid and normal salts; in alkaline solutions, however, it has probably the open form, as the silver salt prepared from such a solution has a composition corresponding to this.

The *free acid* may be obtained, somewhat contaminated with decomposition products, by decomposing the silver salt under water by hydrogen sulphide, care being taken to keep the liquid cool. The solution has an acid, somewhat astringent, taste, and is imperfectly precipitated by alcohol in a gelatinous form, resembling precipitated alumina. This shows the reaction of the salts, but is impure, as caustic alkali causes the evolution of a little ammonia.

Sodium Salts.—As all the sodium salts are amorphous and precipitated by alcohol, in a syrupy or viscous form, it is not easy to obtain any of them pure. The salt prepared in the above manner contains about 5.4 atoms of sodium (analyses I and II) and forms a white, amorphous, sandy powder, which is not hygroscopic, but which slowly absorbs carbon dioxide. Under water it first becomes pasty and then slowly dissolves, with considerable evolution of heat. Salts with 4 or more atoms of sodium invariably contain 2 molecules of water which are retained at 100°.

The *pentasodium* salt, $P_5N_5O_{10}H_5Na_5 + 2H_2O$, may be obtained by adding to the solution of a salt containing a known excess of sodium, nearly enough nitric acid to neutralize the excess and precipitating by alcohol, or by nearly neutralizing with acetic acid, with phenolphthalein as indicator, and precipitating by alcohol. In the latter case, however, there is a slight deficiency of sodium (analyses III. and IV.) The normal salt has a strongly alkaline reaction and loses some alkali by repeated precipitation by alcohol.

For analysis the salts were dried at 100°.

	Calculated for $P_5N_5O_{10}H_5Na_5+2H_2O$.	I.	II.	III.	IV.
			Found.		
P	28.64	28.23	28.24	29.10	29.13
N	12.96	12.90	12.86	13.29	13.22
Na	21.27	22.74	22.64	21.54	20.77

I and II were precipitated directly from alkaline solution.

I. $P : N : Na = 5 : 5.02 : 5.42$.

II. $P : N : Na = 5 : 5.03 : 5.40$.

III. and IV. were precipitated from a solution neutralized with acetic acid and phenolphthalein.

III. $P : N : Na = 5 : 5.03 : 4.75$.

IV. $P : N : Na = 5 : 5.02 : 4.80$.

The *tetrasodium salt*, $P_5N_5O_{10}H_5.Na_4H + 2H_2O$, is obtained by dissolving the crude salt in water with its own weight of 80 per cent. acetic acid and precipitating twice by alcohol. It resembles the normal salt, but has neutral reaction.

It gave after drying at 100° :

	Calculated for $P_5N_5O_{10}H_5.Na_4H+2H_2O$.	Found.
P	29.85	30.02
Na	17.74	17.71

$P : Na = 5 : 3.97$.

Salts with still less alkali can be obtained by precipitating the crude salt by alcohol from a nitric acid solution. This precipitate is viscous rather than syrupy as with the salts with 4 and 5 atoms of sodium. Salts with 5 or more atoms of sodium can be kept indefinitely without alteration and do not evolve ammonia with alkalies, but those with less gradually decompose.

Barium Salt.—A solution of the sodium salt gives, with barium chloride, a voluminous precipitate of unknown composition, insoluble in water and acetic acid.

Magnesium Salts.—Pentametaphosphimic acid forms several salts with magnesium alone, as well as double salts with magnesium and other metals.

A solution of the sodium salt, strongly acidified with acetic acid, gives, with magnesium salts, a voluminous amorphous precipitate, nearly insoluble in water and but slightly more soluble in strong acetic acid. The composition of this, after drying at 100°, approximates to $P_5N_6O_{10}H_5.Mg_2H + 5H_2O$.

	Calculated for $P_5N_6O_{10}H_5.Mg_2H+5H_2O$.	Found. I.	II.
P	29.26	28.82	29.05
Mg	9.16	9.52	10.10

I. $P : Mg = 5 : 2.11$.

II. $P : Mg = 5 : 2.22$.

A considerable portion ot the acid remains in solution how-

ever, even in the presence of a large excess of the precipitant, in combination with less than 2 atoms of magnesium, and can be precipitated by alcohol as a salt soluble in water. If this insoluble magnesium salt be dissolved in dilute nitric acid and ammonia added to incipient precipitation, the solution, after filtering, contains essentially the primary salt $(P_5N_5O_{10}H_9)_2Mg$; from this solution silver nitrate throws down an amorphous magnesium silver salt with a varying amount of silver. The primary salt is easily soluble in water and is remarkably stable, giving no precipitate with ammonia, sodium hydroxide or carbonate, even on boiling. The magnesium can be removed only by adding to its solution ammonia and an alkaline phosphate. On boiling in neutral or acetic acid solution, however, a precipitate of the 2-atom salt at once forms. Even the latter dissolves in boiling sodium carbonate solution.

Indications of an intermediate salt were observed, but it could not be isolated in pure condition.

Silver Salts.—The silver salts of the phosphorus-nitrogen acids are invariably free from water, and it is upon these, therefore, that the formulas of the acids themselves are based. There is no difficulty in obtaining normal silver tri- and tetra-metaphosphimates of theoretical composition, and their crystalline nature affords a guarantee of their homogeneity. The same difficulty is encountered with the silver pentametaphosphimates, however, as with the sodium salts; they are amorphous flocculent precipitates, the composition of which corresponds to a definite formula only when they are formed under special conditions. In this case, as in others in this paper, the actual percentage composition expresses very little, if compared with the calculated composition of a definite salt. It is therefore better to express the results of the analysis in a molecular formula based on the atomic ratios of phosphorus, nitrogen, and silver, as actually determined; a comparison of the percentage composition found, with that calculated for salts of the lactam and open chain acids containing phosphorus and silver in the same ratio, then shows at once to which of these acids the salt is to be referred.

The composition of the precipitates depends altogether on the relative amounts of the reacting bodies and even the free

acid can be almost completely precipitated, provided a sufficient excess of silver nitrate be used. The preparations analyzed were made by precipitating a solution of 1 gram sodium salt in 50 cc. water with 55 cc. $\frac{1}{2}$-normal silver nitrate solution. To the sodium salt was added enough nitric acid to produce a salt of known composition. Under these conditions it was found that a salt with 4 atoms of sodium gives very nearly the normal salt, $P_5N_5O_{10}H_5Ag_5$, (analyses III., IV., VI.), the number of equivalents of silver in the precipitate always exceeding the number of equivalents of sodium. Up to 5 atoms of silver the precipitates are white; with more silver they become more and more yellow in proportion to the amount of silver they contain. An excess of 0.3 atom over the normal imparts a perceptible yellow tint. The salts are unaffected by light or by heating at 100°, and are decomposed by cold caustic alkalies[1] with separation of silver oxide.

In the following table the molecular formulas given are based on the ratio of phosphorus to silver actually determined and referred to the acids $P_5N_5O_{10}H_{10}$ and $P_5H_6O_{11}H_{12}$. A comparison shows that the salts are derivatives of the former, a true metaphosphimic acid. The salts were dried at 100°.

	Ratio P : N : Ag.		P.	N.	Ag.
I.	5 : 5.02 : 5.18	$P_5N_5O_{11}H_{5\cdot82}Ag_{5\cdot18}$	16.03	7.26	57.80
		$P_5N_5O_{10}H_{4\cdot82}Ag_{5\cdot18}$	16.34	7.39	58.88
		Found	16.31	7.41	58.76
II.	5 : 5.06 : 5.32	$P_5N_5O_{11}H_{5\cdot68}Ag_{5\cdot32}$	15.79	7.15	58.45
		$P_5N_5O_{10}H_{4\cdot68}Ag_{5\cdot32}$	16.09	7.28	59.55
		Found	16.04	7.35	59.37
III.	5 : 5.04 : 4.95	$P_5N_5O_{11}H_{7\cdot05}Ag_{4\cdot95}$	16.45	7.45	56.66
		$P_5N_5O_{10}H_{5\cdot05}Ag_{4\cdot95}$	16.77	7.59	57.77
		Found	16.75	7.64	57.69
IV.	5 : 4.96 : 4.96	$P_5N_5O_{11}H_{7\cdot04}Ag_{4\cdot96}$	16.45	7.45	56.66
		$P_5N_5O_{10}H_{5\cdot04}Ag_{4\cdot96}$	16.77	7.59	57.77
		Found	16.77	7.53	57.82
V.	5 : 5.04 : 5.15	$P_5N_5O_{11}H_{5\cdot85}Ag_{5\cdot15}$	16.09	7.28	57.65
		$P_5N_5O_{10}H_{4\cdot85}Ag_{5\cdot15}$	16.40	7.42	58.75
		Found	16.32	7.45	58.46
VI.	5 : 5.05 : 4.97	$P_5N_5O_{11}H_{7\cdot03}Ag_{4\cdot97}$	16.42	7.43	56.78
		$P_5N_5O_{10}H_{5\cdot03}Ag_{4\cdot97}$	16.74	7.57	57.89
		Found	16.62	7.59	57.51

[1] $P_5N_5O_5H_3Ag_3$ is scarcely affected by boiling with strong caustic potash and $P_4N_4O_8H_4Ag_4$ is scarcely affected in the cold, but is at once decomposed on boiling.

Tri- and tetrametaphosphimic acids, when precipitated from ammoniacal solution by excess of silver nitrate, gave amorphous yellow salts of the composition $P_3N_3O_7H_2Ag_6$ and $P_4N_4O_9H_2Ag_6$ respectively.[1] These are salts of the open chain acids. A similar salt is obtained by precipitating an ammoniacal solution of pentametaphosphimic acid by silver nitrate, but in accordance with its less acid properties the quantity of silver does not reach 10 atoms, being in the specimen analyzed only 8.76 atoms, but the figures correspond closely to a derivative of *amidotetrimidopentaphosphoric acid*, $P_5N_5O_{11}H_{12}$, rather than pentametaphosphimic acid. Dried at 100° it gave :

Ratio P : Ag.

$$5 : 8.76 \begin{cases} P_5N_5O_{11}H_{2.24}Ag_{8.76} & 11.49 & 70.04 \\ P_5N_5O_{10}H_{1.24}Ag_{8.76} & 11.64 & 70.98 \\ \text{Found} & 11.48 & 70.03 \end{cases}$$

It appears, therefore, that in alkaline solution the metaphosphimic acids become open-chain acids, just as lactones and lactams give γ- and δ-oxy- and amido-acids. On drying at 100°, the yellow silver salts become gray without loss of weight, probably owing to separation of silver oxide. This is perhaps due to a tendency to revert to the lactam form, with separation of silver oxide, rather than water.

Decomposition of Pentametaphosphimic Acid.—Pentametaphosphimic acid is markedly more stable in acid solution than trimetaphosphimic acid. In my paper on the latter I described in detail its decomposition products when acted on by nitric acid.[2] Under identical conditions the rate of decomposition of pentametaphosphimic acid was found to be very much slower. On account of this greater stability the action of hot acetic acid gives more satisfactory results. No attempt was made to isolate all the products, as these are numerous and the analytical difficulties considerable. The following were identified :

[1] This JOURNAL, 18, 651, 788. The formula $P_4N_4O_9Ag_6$ was there ascribed to the persilver salt of tetrametaphosphimic acid ; a recalculation of the analyses in the above manner, however, shows that they correspond much more closely to the open form $P_4N_4O_9H_2Ag_6$, with a slight deficiency of silver.

[2] This JOURNAL, 18, 653.

Tetrametaphosphimic acid, $P_4N_4O_8H_8$.
Triimidotetraphosphoric acid, $P_4N_3O_{10}H_9$.
Diimidotriphosphoric acid, $P_3N_2O_8H_7$.
Orthophosphoric acid, H_3PO_4.

5 parts sodium pentametaphosphimate are dissolved in 15 parts water, 5 parts strong acetic acid added, and the solution heated in the water-bath. The separation of a crystalline precipitate of acid sodium tetrametaphosphimate begins in about fifteen minutes and continues for perhaps eight hours, at the end of which time the solution gives no precipitate with magnesium chloride, indicating the absence of pentametaphosphimate. The sodium tetrametaphosphimate, being insoluble in a solution of sodium salts, is completely precipitated. It is filtered off and washed a little with a saturated sodium acetate solution. The filtrate is concentrated to about one-half with addition of about 5 parts solid sodium acetate, whereby sodium triimidotetraphosphate separates, in the form of flat prisms or plates, which are washed with a little saturated sodium acetate solution and purified by dissolving in water and precipitating by alcohol, or by adding solid sodium acetate to their hot solution. On further concentrating the filtrate, large plates are often obtained, which give, with silver nitrate and nitric acid, a crystalline precipitate of the characteristic silver diimidotriphosphate, $P_3N_2O_8H_4Ag_3$.[1] No satisfactory and certain method can be given for the separation of these two acids.

The sodium tetrametaphosphimate thus obtained usually has the form of spindles, but, when well developed, consists of brilliant double pyramids. It had not been observed at the time of writing the paper on tetrametaphosphimic acid. It is obviously an acid sodium salt, as it is formed only in the presence of acetic acid or a limited amount of a stronger acid. It was also obtained directly from the original sample of the acid, but was not analyzed, as it is difficult to obtain a sufficient quantity uncontaminated by the free acid. It is moderately soluble in water, but almost insoluble in solutions of sodium salts and is highly characteristic of this acid. The crude salt was dissolved in ammonia, with the addition of

[1] This JOURNAL, **18**, 657.

some ammonium nitrate, and precipitated by nitric acid as $P_4N_4O_6H_6(NH_4)_2$.[1] The precipitation is almost quantitative. This pure salt was dissolved in ammonia, largely diluted, and, after acidifying with nitric acid, precipitated by an excess of silver nitrate in the form of the characteristic $P_4N_4O_6H_4Ag_4$. This gave:

	Calculated for $P_4N_4O_6H_4Ag_4$.	Found.
P	16.68	16.88
N	7.55	7.56
Ag	58.03	57.51

The free acid was obtained by decomposing the silver salt with hydrochloric acid in the characteristic form of difficultly soluble needles. It gave:

	Calculated for $P_4N_4O_6H_8 + 2H_2O$.	Found.
P	35.22	35.08
N	15.94	15.75

A comparison of the acid potassium, sodium, and ammonium salts and neutral ammonium salt with those prepared from a sample of tetrametaphosphimic acid from tetraphosphonitrilic chloride showed them to be identical in form. The yield of tetrametaphosphimic acid appears to be nearly independent of proportions and concentration, and was about 12 per cent. of that required by the equation

$$P_5N_5O_{10}H_{10} + 2H_2O = P_4N_4O_6H_8 + NH_4H_2PO_4.$$
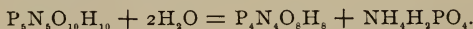
Triimidotetraphosphoric Acid, $PO(OH)_2.NH.POOH.NH.-POOH.NH.PO(OH)_2$.—The sodium salt of this, the third member of the imidophosphoric acid series obtained,[2] crystallizes well in small rhombic or six-sided plates. The several specimens obtained were not analyzed, but converted into the silver salt. By analogy with $P_3N_2O_8H_7$, there can be little doubt that it is the acid salt, $P_4N_3O_{10}H_6Na_4$. It is easily soluble in water, but almost insoluble in saturated sodium acetate solution or dilute alcohol. It gives a precipitate with magnesium nitrate only on adding ammonia and ammonium chloride, when a voluminous precipitate is obtained, which, on standing, slowly changes to minute crystalline spherules.

[1] This JOURNAL, **18**, 786.   [2] *Ibid*, **18**, 635, 653.

Silver Triimidotetraphosphate, $P_4N_3O_{10}H_5Ag_4$, is obtained as a voluminous amorphous white precipitate by adding silver nitrate to a solution of the sodium salt faintly acidified with nitric acid. On long standing under its mother-liquor it becomes crystalline and this change occurs in a few moments on washing the precipitate, shrinking to a heavy, sandy, crystalline powder, a very characteristic behavior. The same change can be observed under the microscope in the partially washed salt, the amorphous portion changing to minute particles showing active Brownian movement, which aggregate to prisms which are long and pointed and often tufted at the ends, and which cannot be distinguished in appearance from silver tetrametaphosphimate. From a decidedly acid solution the salt is deposited slowly and without the intermediate amorphous form.

The salt gave after drying at 100°:

	Calculated for $P_4N_3O_{10}H_5Ag_4$.	I.	Found. II.
P	16.26	16.43	16.48
N	5.52	5.62	5.55
Ag	56.58	56.61	57.18

I. P : N : Ag = 4 : 3.03 : 3.96.

II. P : N : Ag = 4 : 2.98 : 3.99.

Triimidotetraphosphoric acid could not be obtained from tetrametaphosphimic acid, being much less stable than the latter. It is therefore probably derived from the breaking-down of the chain of phosphorus and nitrogen atoms formed by the hydrolysis of the pentametaphosphimic ring.

Hexametaphosphimic Acid,

$$NH \Big< \begin{matrix} POOH.NH.POOH.NH.POOH \\ POOH.NH.POOH.NH.POOH \end{matrix} \Big> NH.$$ —This is the lactam of amido-pentimidohexaphosphoric acid,

$$NH \Big< \begin{matrix} POOH.NH.POOH.NH.PO \big< \begin{matrix} OH \\ NH_2 \end{matrix} \\ POOH.NH.POOH.NH.PO(OH)_2 \end{matrix} \Big. .$$
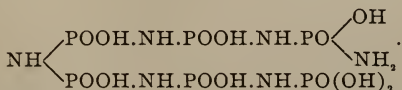
It is obtained as sodium salt by saponifying hexaphosphoni-trilic chloride in ethereal solution by sodium hydroxide in the

manner above described. In neutral or acid solution it has the lactam form, as shown by the composition of the silver salt, but in alkaline solution it has presumably the open form. The *free acid* obtained in solution by decomposing the silver salt under water by hydrogen sulphide has an astringent rather than acid taste, and cannot be obtained pure in the solid form, as it is not precipitated by alcohol, and the solution, on evaporating, undergoes much decomposition, leaving a gummy residue.

Sodium Hexametaphosphimate, $P_6N_6O_{12}H_6Na_6 + 2H_2O$.— The properties of this salt are essentially the same as those of the corresponding pentametaphosphimate. When containing an excess of alkali it is stable, but with a deficiency, it decomposes more or less rapidly. A salt of approximately normal composition can be obtained by adding to the solution of a preparation with more than 6 atoms of sodium enough nitric acid to neutralize the excess and precipitating by alcohol (analyses III. and IV.) .In the following table the results are expressed in formulas based on the determined ratio P : Na. The samples were dried at 100°.

Ratio P:N:Na.		P.	N.	Na.
I. 6:6.02:6.35	$P_6N_6O_{12}H_{5.65}Na_{6.36}+2H_2O$	28.62	12.95	22.50
	Found	28.55	12.96	22.45
II. 6: ... :6.46	$P_6N_6O_{12}H_{5.54}Na_{6.46}+2H_2O$	28.51	....	22.80
	Found	28.31	....	22.63
III. 6:6.04:5.93	$P_6N_6O_{12}H_{6.07}Na_{5.93}+2H_2O$	29.02	13.14	21.31
	Found	29.13	13.27	21.38
IV. 6:6.05:5.94	$P_6N_6O_{12}H_{6.06}Na_{5.94}+2H_2O$	29.02	13.14	21.31
	Found	29.16	13.29	21.43
V. 6: ... :4.60	$P_6N_6O_{12}H_{7.40}Na_{4.60}+2H_2O$	31.05	....	17.70
	Found	30.89	....	17.60

I. and II. precipitated from solution containing excess of alkali.

III. and IV. from solution in which excess over 5 Na had been neutralized.

V. from solution in large excess of acetic acid.

Magnesium Salt.—A solution of the sodium salt, precipitated by magnesium nitrate in the presence of acetic acid, under exactly the same conditions as were observed in preparing

the corresponding pentametaphosphimate, gave a salt which closely resembles the latter, but which does not approximate to any definite formula (found P : Mg = 6 : 2.43). The precipitation is by no means complete, much remaining in solution as a salt which can be precipitated by alcohol, which is not decomposed by boiling with alkalies, and which, in general, resembles the primary salt of pentametaphosphimic acid.

Silver Hexametaphosphimate, $P_6N_6O_{12}H_6Ag_6$.—The silver salt, prepared from the sodium salt, varies in composition with the relative amounts of the reacting bodies and with the amount of sodium. It was obtained of normal composition by dissolving 1 gram sodium salt in 50 cc. water, adding enough nitric acid to produce a salt with 5.75 atoms of sodium, and precipitating by 50 cc. $\frac{1}{5}$-normal silver nitrate (analyses III. and IV.). It resembles the corresponding pentametaphosphimate, but is somewhat more gelatinous. Any excess of silver over 6 atoms tends to give it a yellow color. It is decomposed in the cold by caustic potash with separation of silver oxide. The analyses given in the following table of preparations dried at 100°, show that it is derived from the true hexametaphosphimic acid, $P_6N_6O_{12}H_{12}$.

Ratio P : N : Ag.		P.	N.	Ag.
I. 6 : 6.08 : 5.65	$P_6N_6O_{13}H_{6.35}Ag_{5.65}$	16.97	7.68	55.60
	$P_6N_6O_{12}H_{6.35}Ag_{5.65}$	17.26	7.81	56.53
	Found	17.23	7.89	56.48
II. 6 : ··· : 6.21	$P_6N_6O_{13}H_{7.79}Ag_{6.21}$	16.09	···	57.97
	$P_6N_6O_{12}H_{5.79}Ag_{6.21}$	16.35	···	58.89
	Found	16.29	···	58.64
III. 6 : 5.99 : 5.98	$P_6N_6O_{13}H_{6.02}Ag_{5.98}$	16.44	7.44	57.02
	$P_6N_6O_{12}H_{6.02}Ag_{5.98}$	16.71	7.56	57.95
	Found	16.70	7.54	57.90
IV. 6 : 6.04 : 6.02	$P_6N_6O_{13}H_{7.98}Ag_{6.02}$	16.38	7.41	57.18
	$P_6N_6O_{12}H_{6.98}Ag_{6.02}$	16.65	7.54	58.02
	Found	16.57	7.54	57.80

A yellow salt is obtained by precipitating the ammoniacal solution by silver nitrate.

Decomposition of Hexametaphosphimic Acid.—The sodium salt heated with acetic acid gives tetrametaphosphimic acid, which was isolated in the manner described above. The yield is 30 per cent. of that required by

$$P_6N_8O_{12}H_{12} + 4H_2O = P_4N_4O_8H_8 + 2NH_4H_2PO_4.$$
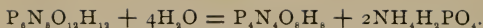
After purifying, it was converted into the silver salt which gave:

	Calculated for $P_4N_4O_8H_4Ag_4$.	Found.
P	16.68	16.63
N	7.55	7.50
Ag	58.03	57.58

$P : N : Ag = 4 : 3.99 : 3.98$.

Comparison of the crystals of free acid and of the acid and neutral ammonium salts, acid potassium salt, neutral sodium salt, and silver salt with similar preparations made from tetraphosphonitrilic chloride showed that they were identical.

The decomposition products were not further studied.

Amidoheximidoheptaphosphoric Acid, $P_7N_7O_{15}H_{18}$.

The saponification of heptaphosphonitrilic chloride is effected in the usual manner with sodium hydroxide. As before pointed out, this acid does not give the lactam, heptametaphosphimic acid, even in acid solution, the silver salt having the composition of a salt of the open-chain acid.

Sodium Salt.—The properties of this salt are similar to those of sodium penta- and hexa-metaphosphimate. Dried *in vacuo* and at 100° it gave:

$$P : Na = 7 : 7.43.$$

	Calculated for $P_7N_7O_{15}H_{8.57}Na_{7.43} + 2H_2O$.	Found.
P	28.16	28.31
Na	22.19	22.31

Silver Salt, $P_7N_7O_{15}H_9Ag_7$.—To obtain a salt of normal composition 1 gram sodium salt is dissolved in 50 cc. water, enough nitric acid is added to form a salt with 6.85 atoms of sodium and precipitated by 50 cc. $\frac{1}{5}$-normal silver nitrate. More sodium or silver nitrate gives a salt richer in silver. The salt forms a white semigelatinous precipitate, which dries *in vacuo* to translucent brittle lumps which were pulverized, dried again *in vacuo* and then carefully to constant weight at 100°.

Ratio P : N : Ag.		P.	N.	Ag.
I. 7 : ⋯ : 6.93	$P_7N_7O_{15}H_{9.07}Ag_{6.93}$	16.55	⋯	56.99
	$P_7N_7O_{14}H_{7.07}Ag_{6.93}$	16.77	⋯	57.77
	Found	16.44	⋯	56.61
II. 7 : ⋯ : 7.21	$P_7N_7O_{16}H_{6.79}Ag_{7.21}$	16.17	⋯	57.97
	$P_7N_7O_{14}H_{6.79}Ag_{7.21}$	16.40	⋯	58.76
	Found	16.21	⋯	58.09
III. 7 : ⋯ : 7.08	$P_7N_7O_{15}H_{6.92}Ag_{7.08}$	16.35	⋯	57.51
	$P_7N_7O_{14}H_{6.92}Ag_{7.08}$	16.57	⋯	58.30
	Found	16.27	⋯	57.27
IV. 7 : 7.04 : 7.03	$P_7N_7O_{16}H_{6.97}Ag_{7.03}$	16.41	7.43	57.35
	$P_7N_7O_{14}H_{6.97}Ag_{7.03}$	16.64	7.53	58.16
	Found	16.35	7.44	57.14

These figures show, beyond question, that the acid has the open form $P_7N_7O_{15}H_{16}$.

The decomposition of the sodium salt by acetic acid gives rise to a considerable amount of tetrametaphosphimic acid, characterized by its crystalline form and that of its salts.

Higher Acids.—Of the higher acids of the series but little can be said. The oil remaining over from preparation of chloronitrides and which has a mean molecular weight nearly corresponding to $P_{11}N_{11}Cl_{22}$,[1] on saponification gives a mixture of sodium salts which are precipitated by alcohol in a decidedly viscous form, and which are decomposed by acids, give tetrametaphosphimic, diimidotriphosphoric, and triimido-tetraphosphoric acids. They were not further investigated.

Amides of Metaphosphimic Acids.

Amides of $P_3N_3O_3H_6$.—Strong ammonia gas acts slowly on a solution of $P_3N_3Cl_6$ in absolute ether, the product being at first ammonium chloride and the chloramide,[2] $P_3N_3\Big\langle{}^{Cl_4}_{(NH_2)_2}$.

This remains in solution and is gradually attacked further, but is the only product of the reaction which is soluble in ether; by further action of ammonia the chlorine is further substituted, but never completely, and the reaction product is thrown down, mixed with ammonium chloride. On washing this with alcohol, dissolving in water, and treating with

[1] This JOURNAL, **19**, 793.   [2] *Ibid*, **17**, 286.

enough silver nitrate to precipitate the chlorine, a solution is obtained which, by fractional precipitation with silver nitrate, gave the silver salt of an amide with the ratio $P : N : Ag =$ 3 : 6.27 : 2.01.   An ethereal solution of $P_3N_3\left\langle\begin{array}{l}Cl_4\\(NH_2)_2\end{array}\right.$, shaken with sodium hydroxide, gives the sodium salt of the diamide of trimetaphosphimic acid, from which the chlorine may be removed by neutralizing with nitric acid and adding the calculated amount of silver nitrate. From the filtrate an amorphous silver salt may be precipitated which gave the ratio $P : N : Ag = 3 : 4.88 : 3.51$. If $P_3N_3Cl_6$, $P_4N_4Cl_8$, or $P_5N_5Cl_{10}$, in ethereal solution is shaken with ammonia of sp. gr. 90, a strong reaction occurs at first, whereby a portion of the chlorine is replaced. On shaking two or three hours, the remainder is removed. The excess of ammonia was removed from the aqueous solution by blowing air through and the chlorine precipitated by the theoretical amount of silver nitrate. The ammonium salts of the amides thus obtained were thrown down by alcohol as syrups which cannot be hardened under absolute alcohol. If these solutions are precipitated by silver nitrate, after adding a little ammonia, amorphous white precipitates of the amido silver salts are obtained, which do not show a constant composition. Analysis gave the following atomic ratios:

Amide from P_3N_3Cl—$P : N : Ag = \begin{cases} 3 : 5.80 : 2.20 \\ 3 : 5.96 : 3.36 \\ 3 : 6.54 : 3.08 \end{cases}$

Amide from $P_4N_4Cl_8$—$P : N : Ag = \begin{cases} 4 : 8.80 : 4.82 \\ 4 : 9.28 : 4.03 \end{cases}$

Amide from $P_5N_5Cl_{10}$— $P : N : Ag = 5 : 10.16 : 2.64$

From these figures it appears that the amides are of very varying composition. As they are amorphous and very unstable, it is unlikely that any definite bodies can be obtained in this way. The silver salts are turned yellow by potassium hydroxide, a portion of the amide going into solution and a salt with a higher proportion of silver being formed.

THE ETHERS OF TOLUQUINONEOXIME AND THEIR BEARING ON THE SPACE ISOMERISM OF NITROGEN.

By John L. Bridge and Wm. Conger Morgan.

In an article on the ethers of quinoneoxime (isonitrosophenol) published by one of us,[1] it was stated, that when boiled with alcohol, the benzoyl ether of quinoneoxime dichloride gave two monochlor substitution-products. Naturally it was supposed that the chlorine atom occupied, in the one, an ortho position and in the other, a meta position to the radical NOR, the reaction being :
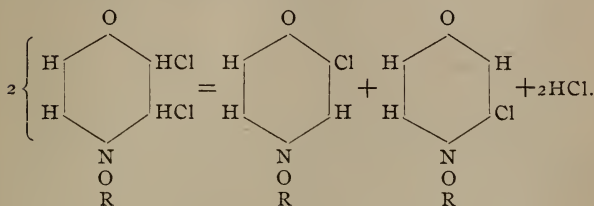
It was also found that these same isomers were formed when monochlorquinone was treated with hydroxylamine hydrochloride, and the sodium salt of the chlorquinoneoxime thus formed, treated with benzoyl chloride.

The preceding explanation regarding the splitting off of hydrochloric acid from the dichloride is not in accord with results of work done by Kehrman,[2] published in his article on the influence of radicals in the action of hydroxylamine on quinones, in which he generalizes the results of his observations in the statement that the presence of a radical attached to the ring so much lessens the replaceability of the quinone oxygen atom neighboring to the radical that the principal part, if not the whole of the resulting product, is a meta-substituted quinoneoxime. The work of his former article has

[1] Ann. Chem. (Liebig), 277, 79.
[2] Ber. d. chem. Ges., 21, 3315; J. prakt. Chem. [2], 40, 258.

been repeated by Kehrman,[1] who finds the same isomeric benzoyl ethers of monochlorquinoneoxime ; but, believing that observations of their behavior indicate the substantiation of his rule, he states that both these ethers have the chlorine atom in the meta position to the oximido group, and attributes their difference to space isomerism of nitrogen, writing the reaction thus :
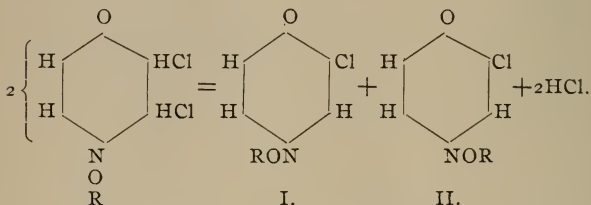
Kehrman designates the compound represented by symbol I. as ''chlorquinonemetaantioxime ether'' and II. as ''chlorquinone-metasynoxime ether.'' The question as to whether the chlorine atom occupies the same position in both compounds could be definitely settled if ortho- and metachlorphenols could be changed to the corresponding chlorquinoneoximes or so-called isonitrosophenols. This transformation has, however, unfortunately not yet been accomplished, and repeated efforts to obtain the corresponding bromquinoneoximes have resulted in failure, orthobromphenol not being attacked by nitrous acid or amyl nitrite.

The toluquinoneoximes obtained by the action of nitrous acid on ortho- and metacresol, we have taken up for study as being the most closely analogous compounds in which the position of the side groups is definitely known, believing that by an examination of these bodies, light may be thrown upon the nature of the others.

When orthocresol is acted upon by nitrous acid, a toluquinonemetaoxime is formed according to the following reaction :

[1] Ann. Chem. (Liebig), **279**, 27.
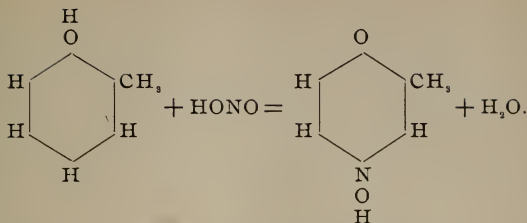
The metacresol forms similarly a corresponding orthooxime :
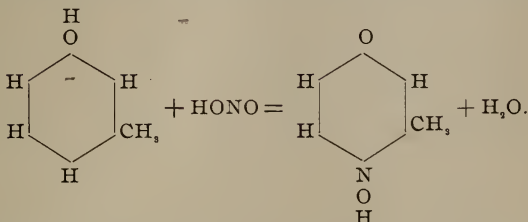
The benzoyl ethers of the toluquinoneoximes prove to be exceedingly well fitted to characterize these bodies since they are formed from the oximes in quantitative proportions, are easily crystallized, and readily distinguished from each other.

The benzoyl ether of toluquinoneorthooxime produced from metacresol, crystallizes in light brownish-yellow crystals, melting at 177° C. and appearing under the microscope as long rectangular blades, suggesting the orthorhombic system. The benzoyl ether of toluquinonemetaoxime produced from orthocresol is obtained in the form of yellow crystals which begin to soften at about 150° and do not melt entirely until at about 190°. Subjected to fractional crystallization, a portion of the metaoxime so readily obtained consisting of branching needle-like crystals, melting at 193° C. These, as well as lower-melting fractions, can be readily distinguished from the orthooxime by their less regular appearance under the lens, as well as by their crystal habit, tending to produce curved forms.

The marked difference in the form and habit of the crystals

of the benzoyl ethers of the ortho- and metatoluquinone oximes makes it possible to study carefully the product of the action of toluquinone on hydroxylamine. Goldschmidt and Schmidt[1] have shown that the principal product of this reaction is toluquinonemetaoxime. This they demonstrated by oxidizing to a dinitro compound ; but as some of the theoretically possible nitro-derivatives of the cresols are not known, this method can scarcely be considered to prove conclusively the absence of toluquinoneorthooxime. We have, therefore, studied further the product of the action of hydroxylamine on toluquinone by the aid of the benzoyl ethers. When the sodium salt of the oxime thus formed was treated in alcoholic solution with benzoyl chloride, and the benzoyl ether obtained was subjected to fractional crystallization, not a trace of the orthooxime ether, crystallizing in blades and melting at 177° C., was found. This proves that when toluquinone is treated with hydroxylamine the whole of the resulting product is toluquinonemetaoxime. The inference is plain that Kehrman's rule concerning the influence of side-chains, attached to the ring in quinones, upon the entering oximido radical is quantitatively true in this case ; and similar indications furnished by the corresponding methyl ethers, as will appear later, strengthen this conclusion.

As has been previously shown, the benzoyl ether of the metaoxime does not consist of a single compound, but is a mixture. The body melting at 193° C. is readily separated in considerable quantities, while the remainder consists of a very intimate mixture of this body with one of much lower melting-point, separated, if it can be separated at all, only with the greatest difficulty. By concentration of the mother-liquor from which the high-melting fractions have been obtained, and carefully crystallizing, fractions may be separated melting almost completely at temperatures, varying with the fraction, between 130° and 150° C. Repeated crystallizations separated each fraction into portions melting, on the one hand, always considerably higher, and, on the other hand, often somewhat lower, and ordinarily no definite body of low melting-point could be isolated. Twice, however, a nearly

[1] Ber. d. chem. Ges., **17**, 2063.

complete separation seemed to have been obtained. Thus, from fractions melting between 140° and 150°, a few short, thick prisms melting once at 142° and again at 144° C. separated, leaving the compound which melts at 193°. Of these crystals there was not enough for a combustion, but an analysis of a fraction melting almost completely at 137° gave figures which show without doubt that this portion had the same percentage composition as the body melting at 193°. If we are to regard the product as it is first obtained as a mixture of two ethers, and consider that 142°–144° is the melting-point of the lower body, we can account for the melting of fractions below 142° on the ground that mixtures may have a lower melting-point than either of the component substances. These results were obtained repeatedly from three separate portions of Kahlbaum's C. P. orthocresol, purchased at different times, as well as from toluquinone melting at 67° C. and wholly volatile when exposed to the air.

When the silver salt of toluquinonemetaoxime acts upon methyl iodide, the product is, likewise, not a single ether but a mixture of ethers, softening at 55° and not melting completely below 70°. From it a body melting at 73°–74° C. can easily be separated, but no other compound of definite melting-point or different crystal form could be obtained.

The acetyl compound of toluquinonemetaoxime presents phenomena similar to those of the benzoyl ethers, but in rather more marked degree. The product, as first obtained by the action of acetyl chloride on the silver salt of the oxime, or by acetic anhydride on the oxime itself, begins to soften at 90° and melts completely at 110°. Upon the first recrystallization a distinction in crystal form appears, and a second crystallization of the separated portions gave short, thick prisms melting at 112°–113° C., and some smaller, spherically grouped crystals, melting at 85°–87° C. The extreme difficulty of preparing the acetyl compound prevented further investigation.

In like manner, the benzoyl ether of monobromtoluquinonemetaoxime seems to be a mixture of isomeric bodies. Thus, it was found possible to add two atoms of bromine to the ethers

of toluquinoneoxime forming colorless dibromides corresponding to the dibrom addition-products of quinoneoxime, and these dibromides, when boiled with dilute alcohol, split off hydrobromic acid with the formation of colored monobrom substitution-products. The benzoyl ether of monobromtoluquinonemetaoxime thus formed shows a variation in melting-point similar to that of the ethers previously discussed.

The foregoing facts speak in favor of Kehrmann's theory of space isomerism in the oximes so far as the metaoximes are concerned. On the other hand, there is no evidence to show the presence of isomers in the ethers of toluquinoneorthooxime : the methyl, acetyl, and benzoyl ethers all act as simple substances, each product melting completely at a definite temperature. It is difficult to understand why isomerism should be so much more evident in the ethers of toluquinonemetaoxime than in the ethers of the orthooximes, unless, possibly, the closer proximity of the side-chain to the oximidogroup prevents the formation of a space isomer. There is, however, a remote possibility that isomeric bodies may exist, so similar in properties that they cannot be detected by the ordinary methods.

Experimental Part.

Preparation of the Oximes and their Salts.

The toluquinone-, ortho-, and metaoximes used in the experiments to be described were made in the following manner : To a solution of 10 grams of cresol and 8 grams of potassium nitrite in 900 cc. of water, a solution of 6 grams of concentrated sulphuric acid in 100 cc. of water was added in small portions during the course of half an hour, care being taken that both original solutions should be between 5° and 10° C., and that this temperature be maintained during the mixing. Nearly all of the oxime separates out on standing in ice-water for one to two hours, and after filtering and washing with 200-300 cc. of ice-water, the amount of oxime obtained by extracting the filtered solution with ether is so small that it may be disregarded. The substances were purified by dissolving in a saturated solution of sodium carbonate and filtering into

dilute sulphuric acid, cooled with ice. At this stage it is generally ready for use, but if further purification is desired, it may be accomplished by dissolving the oxime in ether and shaking with animal charcoal. Upon filtering and evaporating, the oxime crystallizes in long, slightly colored needles. The yield is large in both cases, that of the orthooxime being nearly theoretical. As given by Beilstein, toluquinone-*m*-oxime melts at 134° C.; toluquinone-*o*-oxime melts at 155° C.; Beilstein gives 145°–150°.

The silver salt of the metaoxime was made in the following manner: 5 grams of toluquinone-*m*-oxime was dissolved in a solution of sodium hydroxide, a little less than the quantity calculated to form the sodium salt, and this solution was filtered into 500 cc. of water containing $1\frac{1}{3}$ times the calculated amount of silver nitrate. The precipitate comes down in a flocky, gelatinous condition, but goes over into a granular form on heating to 50° C. in a water-bath. When dissolved in the least possible amount of warm dilute ammonia, and the solution precipitated with hydrochloric acid,

0.1006 gram of the substance, dried over H_2SO_4, gave 0.0590 gram AgCl.

	Calculated for $C_7H_6NO_2Ag$.	Found.
Ag	44.23	44.14

The salt is light reddish-brown when first formed, but turns darker on standing or heating. It decomposes when heated to 100° and, when thoroughly dry, is spontaneously inflammable at a temperature above 60°. It is a rather unstable body and cannot be kept long when at all impure.

The silver salt of toluquinone-*o*-oxime was made in the manner described for the preparation of the silver salt of the meta form. The salt falls in the cold as reddish-brown crystals, tending to darken when exposed to light or heat.

Dried over H_2SO_4, 0.2560 gram gave 0.1498 gram AgCl.

	Calculated for $C_7H_6NO_2Ag$.	Found.
Ag	44.23	44.06

Although very similar in all its properties to the silver salt of toluquinone-*m*-oxime, this salt is, like all the ethers of the

ortho form, much more stable than its corresponding meta isomer.

Toluquinone-m-oxime Methyl Ether.

From o-Cresol.—Of the silver salt of toluquinone-*m*-oxime, 2 or 3 grams were suspended in 10–15 cc. of ligroïn and twice the calculated quantity of methyl iodide added. After standing for an hour with frequent shaking, the liquid was filtered off and the residue extracted with a little hot ligroïn. The united ligroïn solutions were allowed to evaporate spontaneously, and the methyl ether came out in large, dark-yellow, hexagonal prisms. A little more may be obtained by allowing the residue to stand for a week with methyl iodide. The yield in any case is small, the best results apparently being obtained by using not more than 2 or 3 grams of the silver salt at one time. After purifying with animal charcoal and recrystallizing from ligroïn, the product obtained softens at 55° yet does not melt completely below 70°. Portions melting at 73°–74° C. were separated by fractional crystallization, and, on analysis,

0.1101 gram of this body, dried over H_2SO_4, gave 0.2582 gram CO_2 and 0.0599 gram H_2O.

0.0881 gram of the substance gave 7.1 cc. N at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	63.96
H	6.00	6.05
N	9.29	9.59

Although fractions were often obtained melting from 55°–60°, no other compound of very definite melting-point could be separated. The methyl ether is very soluble in all organic reagents; in hot ligroïn it is much more soluble than in cold, from which it crystallizes in small bright-yellow prisms.

From Toluquinone.—To a solution of 2 grams of toluquinone in 800 cc. of water, the calculated amount of methoxylamine hydrochloride was added. Yellow crystals began to precipitate in the course of two hours, and at the end of twelve hours the reaction was completed. The liquid was filtered off and

extracted with ether, which, upon evaporation, left behind a yellow crystalline mass. The two portions were united and recrystallized from ligroïn. The yield was very good, being 75 per cent. of the theory. Even after boiling in ligroïn with animal charcoal and recrystallizing several times, the substance acts like a mixture, softening at 58° and melting at 70°. A portion, less soluble than any other, was easily separated, which melted at 73°–74° C. and was identical in all respects with the methyl ether obtained from the silver salt of toluquinone-*m*-oxime made from *o*-cresol.

0.1263 gram, dried over H_2SO_4, gave 0.2962 gram CO_2 and 0.0672 gram H_2O.

0.2952 gram gave 25 cc. N at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	63.96
H	6.00	5.91
N	9.29	10.00

Toluquinonemetaoxime Acetyl Ether.

This ether can be made in two ways: By adding the calculated amount of acetyl chloride, drop by drop, to 2–3 grams of the silver salt suspended in 15–20 cc. of ligroïn or absolute ether, kept cool by ice-water, evaporating at once, and extracting the residue with hot ligroïn; or by heating 1 molecule of the oxime on the water-bath for an hour with 1.5 molecules of acetic anhydride, adding cold water, filtering off the tarry mass which separates, and extracting it with hot ligroïn. The yield by either method is extremely poor, and sometimes after purifying by boiling with animal charcoal, the total product consisted of a few small crystals. By fractional crystallization two portions were separated, the less soluble composed of thick irregular prisms melting at 112°–113° C., and a much smaller fraction of minute, spherically grouped crystals, melting at 85°–87° C. In analyzing the original product unfractioned:

0.0053 gram, dried over H_2SO_4, gave 0.2090 gram CO_2 and 0.0444 gram H_2O.

0.0848 gram gave 5.8 cc. N at 15° C. and 760 mm. pressure.

	Calculated for $C_9H_9NO_3$.	Found.
C	60.30	59.91
H	5.06	5.18
N	7.84	8.01

The acetyl ether is very soluble in alcohol and ether, much less in ligroïn, and very little soluble in water.

Toluquinone-m-oxime Benzoyl Ether.

From o-Cresol.—This ether can be made from the silver salt suspended in absolute ether, or, better, from the sodium salt in alcohol solution. Slightly less than the amount of sodium calculated to form a sodium oxime is dissolved in 100 cc. of alcohol, 2–5 grams of the oxime added, and into the filtered solution slightly more than the theoretical quantity of benzoyl chloride is dropped slowly, the solution being kept cool. The benzoyl ether begins to separate immediately, and after a few moments the alcohol can be filtered off and rejected, as it contains little of the substance. After boiling in alcohol with animal charcoal, when the solution is submitted to fractional crystallization, three-fourths of the crude product can be readily separated in the form of bright-yellow needles melting at 193° C. Upon concentrating the mother-liquor to a small volume and cooling, nearly the theoretical quantity of the benzoyl ether can be recovered. Nothing further was ever obtained save a few flakes of benzoic acid formed by the saponifying action of hydrochloric acid, produced by the slight excess of benzoyl chloride acting on alcohol. When the portion obtained upon concentration was repeatedly fractioned, it could be separated into portions melting approximately at 193°, and others melting almost completely from as low as 135° to 155°. There seemed to be a tendency, however, for these lower fractions to liquefy at 142°–144°, and once, from an alcoholic solution of a fraction melting at 140°–150°, that evaporated at ordinary temperature, short, thick, prismatic crystals separated from the curved needles of the higher melting (193° C.) fraction. These few prisms melted at 144° C. without decomposition. An analysis of the body liquefying at 193° gave the following figures :

0.2277 gram, dried over H_2SO_4, gave 0.5785 gram CO_2 and 0.0945 gram H_2O.

0.2001 gram gave 10 cc. N at 15° C. and 760 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.30
H	4.60	4.61
N	5.82	5.85

An analysis of a fraction melting from 145°–165° gave these percentages :

0.1421 gram, dried over H_2SO_4, gave 0.3635 gram CO_2 and 0.0565 gram H_2O.

0.6726 gram gave 34.1 cc. N at 15° C. and 770 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.74
H	4.60	4.43
N	5.82	6.02

The benzoyl ether is not at all soluble in water or ligroïn, is slightly soluble in cold alcohol, but dissolves readily in ether, chloroform, and glacial acetic acid. The low-melting body seems to be more soluble in alcohol than its higher-melting isomer, but, as nine-tenths of the total product appeared to be the body melting at 193° C., the small proportion of the low-melting compound may account partially for the idea that the latter is more soluble.

From Toluquinone.—The oxime was made according to the method of Goldschmidt and Schmidt,[1] by treating toluquinone in aqueous solution with an excess of hydroxylamine hydrochloride, extracting with ether, and purifying with animal charcoal. From the sodium salt of the oxime thus formed the benzoyl ether was made in the manner previously described. The product is identical with the benzoyl ether made from *o*-cresol. The body melting at 193° C. was readily isolated and analyzed :

0.1002 gram, dried over H_2SO_4, gave 0.2565 gram CO_2 and 0.0452 gram H_2O.

[1] Ber. d. chem. Ges., **17**, 2063.

0.3581 gram gave 17.8 cc. N at 15° C. and 760 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.81
H	4.60	5.01
N	5.82	5.77

By fractional crystallization, low-melting portions were separated, exactly as in the case of the benzoyl ether made from *o*-cresol, except that some fractions were obtained melting partially as low as 129° C. In order to be certain that benzoic acid (m. p. 120° C.) was not unduly lowering these melting-points, these fractions were boiled with water and filtered hot. The filtrate was not acid to litmus and contained only a trace of organic matter. The ethers, when dried, gave the same melting-point as before boiling with water, and, upon recrystallizing from a little alcohol, did not exhibit any change. Furthermore, the benzoyl ether obtained by the usual method, when only 75 per cent. of the theoretical quantity of benzoyl chloride was used, gave fractions beginning to melt at 129° C. Obviously benzoic acid could not be present in these instances.

By slow, spontaneous evaporation of the alcoholic solution of a fraction liquefying at 140°–150° C., a few crystals melting at 142° C., similar to those obtained in the same manner from the oxime made from *o*-cresol, separated from the body melting at 193° C. Since there was not enough of this compound for a combustion, an analysis was made of a fraction melting at 137° C. with the following results :

0.1131 gram, dried over H_2SO_4, gave 0.2901 gram CO_2 and 0.0480 gram H_2O.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.96
H	4.60	4.72

Fractions were frequently obtained melting at about 177° C., and from these attempts were repeatedly made to isolate some of the ortho isomer. None was ever detected under the lens, and fractional crystallization always separated such por-

tions, principally into the body melting at 190° C., and a small fraction melting much lower.

Since the benzoyl ether will decompose into a dark-brown liquid with the evolution of brown fumes of nitrogen oxides when heated above 160° C., it is only by rapidly heating that 193° C. can be observed as a melting-point. This applies also to the bromine addition-products of the benzoates of both the ortho- and metaoximes.

Dibromtoluquinone-m-oxime Benzoyl Ether.

The benzoyl ether was dissolved in chloroform and cooled while the theoretical quantity of bromine was added in small portions. After standing for an hour, the chloroform was evaporated spontaneously, and the light-brown residue recrystallized from glacial acetic acid. It can also be purified by dissolving in fuming nitric acid and pouring into water. On analysis:

0.1437 gram, dried over H_2SO_4, gave 0.2176 gram CO_2 and 0.0339 gram H_2O.

0.1215 gram gave 0.1140 gram AgBr.

	Calculated for $C_{14}H_{11}Br_2NO_3$.	Found.
C	41.90	41.30
H	2.76	2.62
Br	39.87	39.93

The dibromide is insoluble in water, somewhat soluble in cold alcohol, and readily dissolves in chloroform and glacial acetic acid, from which it crystallizes in white prisms melting at 165° C. with decomposition.

Monobromtoluquinone-m-oxime Benzoyl Ether.

When the dibromide is boiled with alcohol hydrobromic acid splits off, two hours being required to complete the process, during which little or no saponification takes place. After recrystallizing from alcohol, a mixture of monobrom compounds is obtained, melting from 155°–170° C. A portion melting with decomposition at 174° C., was separated and analyzed:

0.1208 gram, dried over H_2SO_4, gave 0.2319 gram CO_2 and 0.0345 gram H_2O.

0.0735 gram gave 0.0425 gram AgBr.

	Calculated for $C_{14}H_{10}BrNO_3$.	Found.
C	52.49	52.36
H	3.15	3.17
Br	24.98	24.63

It is very similar in its properties to toluquinone-*m*-oxime benzoyl ether, crystallizing from alcohol in bright-yellow needles.

Toluquinone-o-oxime Methyl Ether.

The methyl ether of toluquinone-*o*-oxime was made from the silver salt and methyl iodide in the same manner as its meta isomer, the yield being somewhat better. Once recrystallized from ligroïn :

0.1247 gram of the ether, dried over H_2SO_4, gave 0.2931 gram CO_2 and 0.0675 gram H_2O.

0.3484 gram gave 27 cc. N. at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	64.10
H	6.00	6.01
N	9.29	9.22

Its properties are almost identical with the methyl ether of the meta form. It crystallizes from ligroïn in long yellow needles, every portion of which, obtained by fractional crystallization, melts at 69° C.

Dibromtoluquinone-o-oxime Methyl Ether.

The methyl ether was dissolved in chloroform, cooled, and the calculated quantity of bromine added. The reaction is completed in twenty minutes, and, on evaporation of the chloroform, the dibromide is left behind as a dirty white mass. Once recrystallized from ligroïn, the substance is ready for analysis:

0.1690 gram, dried over H_2SO_4, gave 0.1877 gram CO_2 and 0.0456 gram H_2O.

0.0744 gram gave 0.0909 gram AgBr.

	Calculated for $C_8H_9Br_2NO_2$.	Found.
C	30.87	30.29
H	2.92	3.00
Br	51.41	52.00

It is insoluble in water but quite soluble in most organic reagents. From ligroïn it crystallizes in white prisms, melting at 112° C.

Toluquinone-o-oxime Acetyl Ether.

This ether was made by Wurster and Riedel[1] from toluquinone-*o*-oxime and acetic anhydride. It can be prepared also from the silver salt and acetyl chloride, the yield being very poor, only a trifle better than its meta isomer, which it closely resembles in its properties.

0.1194 gram, dried over H_2SO_4, gave 0.2666 gram CO_2 and 0.0545 gram H_2O.

0.2389 gram gave 15 cc. N at 15° C. and 760 mm. pressure.

	Calculated for $C_9H_9NO_3$.	Found.
C	60.30	60.89
H	5.06	5.07
N	7.84	7.35

From ligroïn it crystallizes in irregular yellow prisms, melting at 92° C.

Toluquinone-o-oxime Benzoyl Ether.

This ether was made in alcohol solution from the sodium salt in the manner already described for the benzoyl ether of the meta form. The yield is practically theoretical, and, after one recrystallization from alcohol, the product is ready for analysis.

0.1589 gram, dried over H_2SO_4, gave 0.4074 gram CO_2 and 0.0686 gram H_2O.

0.5101 gram gave 26.1 cc. N at 15° C. and 766 mm. pressure.

[1] Ber. d. chem. Ges., **12,** 1799.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.92
H	4.60	4.80
N	5.82	6.04

Although submitted to the most careful fractional crystallization, every particle obtained melted sharply at 177° C., with slight decomposition. From alcohol it crystallizes in light, brownish-yellow blades, which have all the properties of the metaoxime benzoyl ether except that it is a little more soluble in organic reagents.

Dibromtoluquinone-o-oxime Benzoyl Ether.

The benzoyl ether was dissolved in chloroform, bromine added to the cooled solution, and the product recrystallized from glacial acetic acid.

0.2111 gram, dried over H_2SO_4, gave 0.3208 gram CO_2 and 0.0564 gram H_2O.

0.1003 gram gave 0.0924 gram AgBr.

	Calculated for $C_{14}H_{11}Br_2NO_3$.	Found.
C	41.90	41.44
H	2.76	2.97
Br	39.87	39.21

It is insoluble in ligroïn and water and but little soluble in cold alcohol. Fuming nitric acid dissolves it readily, and from the solution it is precipitated unchanged by water. It crystallizes from glacial acetic acid in short, thick, orthorhombic prisms melting at 159° C. with decomposition.

THE KENT CHEMICAL LABORATORY
of YALE UNIVERSITY,
June, 1898.

ON THE CLAIMS OF DAVYUM TO RECOGNITION AS A CHEMICAL ELEMENT.

BY J. W. MALLET.

In the year 1877, the Russian chemist, Sergius Kern, announced[1] that in treating native platinum ore he had detected a new metal of the platinum group, which he proposed to name in honor of Sir Humphry Davy. A brief description

[1] Compt. rend., **85**, 72; Chem. News, **36**, 4, 114, 155, 164; and **37**, 65.

was given of the process by which the separation of the metal was effected, and some of its reactions were described. The metal itself was said to be silvery in appearance, fusible with difficulty by means of the oxy-hydrogen blowpipe, hard, and to some extent ductile, of spec. grav. 9.385 at 25° C. Only 0.27 gram was obtained from 600 grams of the platinum ore, $=$ 0.045 per cent., and in subsequent papers the author spoke of it as still more sparingly obtainable, saying that most of the platinum ore used contained but 0.0008-0.001 per cent., that only a few samples gave as much as 0.035-0.045 per cent., and that the whole quantity of davyum obtained was "so small that no serious experiments could be made." The only report by another chemist on the existence of this claimant for distinct elementary character seems to be a very short paragraph in Valentin's "Course of Qualitative Chemical Analysis (6th edition, 1884), in which the editor, Dr. W. R. Hodgkinson, says that he has obtained a small quantity of the new metal from native platinum, and has found that "it decomposes water in presence of H_2SO_4, the oxide formed scarcely dissolving in the acid"—a very remarkable statement in regard to a metal of the platinum group.

Most compilers of chemical handbooks have either ignored davyum altogether, or have relegated it to mere mention among the sundry "supposed elements," of which the list is not a short one. It is desirable that this list be as far as possible expurgated, and any experiments tending to establish or overthrow belief in the existence of a supposed element have some interest.

The point which seems to make it particularly interesting to decide whether there is such a metal as davyum or not, is the statement by Kern that the atomic mass, as determined in preliminary experiments by Alexejeff, must be near to 154. This would suggest the possible existence in the "periodic" classification of the elements of a hitherto unrecognized element, or more probably a triad of elements, analogous to the triads—ruthenium, rhodium, palladium, and osmium, iridium, platinum,— and having an average atomic mass about

half way between these two sets of three. Thus we should have :

Ruthenium 100.91	?	Osmium 189.55
Rhodium 102.23	Davyum 154. ?	Iridium 191.66
Palladium 105.56	?	Platinum 193.41

It is noteworthy that in Mendeléeff's arrangement of the elements in groups and series, we have representatives of the eighth group in the fourth, sixth and tenth series, but none in the eighth series, a place which would be taken by elements with atomic masses approximately equal to that attributed to davyum. So that, if the existence of davyum were established, it would render probable the subsequent discovery of two more metals analogous to it.

As the best means of securing a favorable chance for investigating the existence or non-existence of the supposed element, I wrote two or three years ago to Mr. George Matthey, F. R. S., of London, knowing the generous readiness to aid scientific research which he and the eminent firm of platinum manufacturers to which he belongs have always shown. I stated to him the object which I had in view, and asked whether he would be willing to let me have the use of such residues from the working on the large scale of native platinum as might most probably yield davyum, any of the already known platinum metals separated therefrom to be returned. His reply was most cordial, and he obligingly offered the free use of such residues as I should designate. The feature in Kern's description of his new element which seemed to offer the best starting-point was the very slight solubility of the double chloride of davyum and sodium, and I suggested to Mr. Matthey that if, without too much trouble or disturbance of the usual course of working native platinum, the solution in *aqua regia* of the crude material, cleared by decantation from the insoluble osmiridium, etc., and by precipitation with ammonium chloride from the bulk of the platinum, could be evaporated to dryness with a large excess of common salt, and the residue redissolved in a minimum of water, any sparingly soluble material left behind by this second solution might be expected to contain the element

sought for, and should be collected and sent to me. He very kindly promised that this should be done, but it was not feasible to take up the matter for some months. Meantime Mr. Matthey informed me that in the precipitation of platinum from certain liquors, a solution of ammonium chloride saturated with sodium chloride was often used, and that by evaporation of the clear solution (after precipitation) colored crystals of impure sodium chloride with a little ammonium chloride were produced ; this crude salt he thought might be worth examination, and he offered to send me some of it. In due time I received about a pound of this rose-colored common salt, and later a specimen of the residue obtained by treating a lot of native platinum as I had suggested—35 kilograms'[1] of Russian platinum mineral had yielded 13 grams of residue, and of this about half was sent me. Mr. Matthey stated in a letter accompanying the sample of residue that the process had been unusually tedious, in consequence of the fact that in the second crystallization, when the liquor was saturated with sodium chloride, such a dense mass of crystals formed to be re-dissolved only by the cautious use of cold water, as to require a very long time for solution and settlement. The two materials for examination, therefore, were this residue, obtained in accordance with my suggestion as to treatment of the complex solution of the metals from native platinum with sodium chloride, and the rose-colored crystals of impure common salt from the regular course of procedure offered me by Mr. Matthey.

It was at once apparent on inspection of the former of these —the residue from special treatment—that it was not likely to be the sodio-chloride of any metal. It was an exceedingly fine gray powder, with minute glistening specks, and proved to be insoluble, not only in water, but in ordinary acids. It was hard enough to readily scratch glass, and even made some minute scratches upon rock crystal, when rubbed on by means of cork or wood. Seen under the microscope it exhibited a multitude of transparent, colorless granules, with

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[1] This quantity, at the lowest proportion reported by Kern, *viz.*, 0.0008 per cent., should have contained 0.280 gram of metallic davyum, or at the highest proportion reported, 0.045 per cent, 15.750 grams.

a smaller proportion of steel-gray or black, opaque and brilliantly lustrous little crystals, most of which were hexagonal plates with (plane) angles of 120°, and a few angles which measured a little more than 127°. Many fragmentary crystals were visible, and a few had the appearance of elongated blades. Many of the perfect crystals, while very minute, were beautifully sharp and well defined. Treatment with gently heated hydrofluoric acid drove off much silicon fluoride, and heating of what remained with concentrated sulphuric acid rendered soluble a small amount of zirconium sulphate with a trace of iron. The residue from the action of both acids was mixed with sodium chloride in fine powder, and at a dull red heat exposed to the action of moist chlorine gas—this, Wöhler's process for decomposing osmiridium, proved easily effective in consequence of the fine state of division of the material, and yielded osmium volatilized mainly as the tetroxide, and iridium with a little rhodium left behind as sodio-chloride. It was evident that the material sent from London consisted merely of such part of the insoluble matter of the native platinum as *aqua regia* had left behind in so extremely fine a state of subdivision that it had remained suspended through the no doubt careful settling and decantation to which the platinum solution had been subjected. It is interesting to find so very dense a substance as osmiridium thus long held in suspension. After deduction of rather more than one per cent. of hygroscopic moisture, the composition of this residue was approximately

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Quartz         40.8
Zircon         15.4          ⎧ Iridium  30.2 ⎫ (decomposition
Osmiridium     43.8 = about ⎨ Rhodium   1.4 ⎬ by chlorine not
               ─────         ⎩ Osmium   12.2 ⎭ quite complete).
               100.0
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The crude common salt in rose-colored crystals dissolved almost completely in water, producing a solution of rather orange or aurora-red color, having a distinct, though not very strong, acid reaction to litmus. Using a minimum quantity of cold water, applied in several successive portions, a minute residue was left undissolved, but a few milligrams

from a couple of hundred grams of the salt, which residue consisted partly of fine light gray matter resembling that already noticed, but chiefly of a buff-colored powder, appearing under the microscope (with a power of 250–450 diameters) as distinctly transparent and crystalline, with the general aspect of minute octahedra and cubo-octahedra ; no colors shown in polarized light. The clear aqueous solution was reduced by a rod of extremely pure zinc, and a little hydrochloric acid. Most of the metallic precipitate thrown down was loose and flocculent, but there was a strong tendency to the formation of a *specular* and pretty firmly adherent deposit on the glass of the beaker and stirring rod. The precipitate, dried at 120° C., represented a little less than 0.2 per cent. of the crude salt taken. This precipitate, which if strongly ignited in the air gave off a slight but unmistakable odor of osmium tetroxide, was redissolved by *aqua regia*, and the solution was mixed with a moderate excess of sodium chloride, evaporated almost to dryness, rediluted with water and again evaporated to remove surplus acid, and finally allowed to stand in the cold for two or three days, the concentration being such that only a little sodium chloride separated out. On decanting, and cautiously removing by water the small remaining surplus of sodium chloride, a little more of a buff-colored residue was obtained, looking, both to the naked eye and under the microscope, like the original residue from the treatment of the crude rose-colored salt with water. The buff-colored material from these two sources —that first obtained having been freed from the light gray powder by washing with a saturated solution of common salt, and decantation—was washed with alcohol, in which it seemed to be practically insoluble, and dried. A little specimen of it dissolved in a large quantity of water. Another small portion, tested spectroscopically, showed the presence of sodium with a trace of potassium. The principal part was dried at 120° C., weighed, and heated to redness in a stream of hydrogen ; the residual metal, washed free of alkaline chloride, was dried and weighed ; it formed 37.1 per cent. of the salt decomposed. Assuming this double chloride to be

anhydrous, sodium to be the only alkaline metal present, and a single metal of the platinum group to be associated with it, the atomic mass of such platinum metal would be 151.5 for the formula Na_2MCl_6, or 165, for the formula Na_3MCl_6. Of these formulæ the former is the more probable, and leads to an approximate value for the atomic mass not very different from that assigned by Kern to davyum. Both determinations were made with quantities altogether too small for any very accurate result.

The general properties of the metallic material thus obtained agreed in the main with those described by Kern, as far as they could be compared by experiments on so minute a scale, and after solution in *aqua regia*, which was effected but slowly and with difficulty, the reactions in the liquid way were pretty nearly such as he obtained. But, although a small part of the solution gave a red coloration with potassium thiocyanate, a reaction pointed out by Kern as among those particularly characteristic of davyum, a simple additional test with potassium ferrocyanide at once showed the presence of iron, though in small amount, thus accounting for the red color. Furthermore, on placing, in the chief portion of the solution, a little lump of sal ammoniac and allowing it to remain until it had dissolved to saturation, a dark brown-red precipitate was formed, from which the ordinary reactions of iridium were obtained, while the remaining liquor, evaporated to dryness and the solid residue ignited, left rhodium, probably not pure, but identifiable by the action upon it of fused potassium acid sulphate. So that the material examined consisted, not of a single distinct metal, but merely of a mixture of iridium and rhodium with a little iron. The whole quantity available was quite insufficient for any exact quantitative analysis, but the very rough approximation to a mean atomic mass indicates that the two metals of the platinum group must have been present in not very unequal quantities.

Of course the results thus obtained, while lending no support to a belief that there is such an element as davyum, do not suffice to disprove its existence. It may, however, be

remarked that in the account given by Kern himself of his
experiments, there are some points tending to increase doubt
as to the conclusion which he reached. Thus, there is, prob-
ably from carelessness, some erroneous statement of facts,
as, for instance, the assertion that *like platinum chloride* the
chloride of davyum forms double salts with ammonium and
potassium chlorides *insoluble in water and easily soluble in abso-
lute alcohol.* It is suggestive that davyum is said to have been
obtained from native platinum in the separation of rhodium
and iridium. There is no allusion to the well-known fact of
the reactions afforded by one of the platinum metals being
modified by the presence along with it of others of this group,
notably true of iridium solutions when containing also
platinum, palladium, or rhodium. It is unsatisfactory to find
the statements that "careful qualitative analyses showed no
presence whatever of iron," and that the author's davyum
"was found to contain no metals of other groups" without
any details being given of the tests by which it was supposed
that these points were established.

On the whole it seems most probable that, in default of
better proof of elementary character than has yet been given,
davyum is to be looked upon as merely a mixture of iridium
and rhodium with a little iron ; and, hence, that we have not
yet reason to believe in the existence of a third triad group
of platinum metals.

UNIVERSITY OF VIRGINIA,
August 20, 1898.

REVIEWS.

THE DISCHARGE OF ELECTRICITY THROUGH GASES. Lectures deliv-
ered on the occasion of the sesquicentennial celebration of Princeton
University. By J. J. THOMSON, Professor in the University of Cam-
bridge. New York : Charles Scribner's Sons. 1898. $1.00.

The authorities of Princeton College, in the fall of 1896, in
honor of its sesquicentennial and to commemorate its trans-
ition from a college into a university, invited some of the noted
scholars of Europe to attend these exercises and to deliver
courses of lectures on their special subjects. Among those
who accepted the invitation were Professors Dowden, of Trin-
ity College, Seth, of Edinburgh, Klein, of Göttingen, and J. J.

Thomson, of Cambridge. The latter delivered four lectures and has now published them in an expanded form with some results obtained since the lectures were delivered. The book is illustrated with diagrams and is in the form of a continuous treatise and not of separate lectures. It is divided into three parts : The Discharge of Electricity through Gases, containing the various methods of electrification of gases ; Photo-electric Effects, under which head he takes up the different forms of sparks, conductivity the arc in hydrogen and the transport of one gas through another ; and Cathode Rays. Under this special form of transmission, to which so much attention is now being given, the author discusses, among other things, the effects produced by these rays, their properties and the influence of outside agents on them, and the theories of the nature of cathode rays. He considers the phenomena best explained on the assumption that the rays are composed of corpuscles in motion, the corpuscle being formed by the breaking up of atoms, a theory which, if sustained, will destroy the theory, held for so long, of the indivisibility of atoms. No further recommendation of this book is necessary than the mention of the name of the author, who is so well known for his scientific investigations and writings. It is a summary in a form suitable for one who is not a specialist.   J. E. G.

JAHRBUCH DER ELEKTROCHEMIE. NERNST UND BORCHERS. Jahrgang 1897. Halle : Wilhelm Knapp. 1898. 15 Marks.

Meyer's Jahrbuch der Chemie contains a brief mention of the investigations, in the different branches of chemistry, carried on each year ; but this science has become specialized to such an extent that it has been found impossible to cover the ground in detail in such a volume, and works devoted to special subjects have been established to supply this need. In 1893 a Jahrbuch der organischen Chemie was started, and in 1894 the development of Electrochemistry had been so great as to necessitate the publication of a Jahrbuch der Elektrochemie to cover all the work in this line. The present volume is the fourth in this series, and its size cannot fail to impress one with the great advance made in this special branch of chemistry within a few years. All the investigations, in the line of electrochemistry, which have been carried out during 1897 are fully treated in this number, which is a valuable addition to those already published.   J. E. G.

A BRIEF COURSE IN QUALITATIVE ANALYSIS. By E. A. CONGDON, PH.B., F.C.S. Professor of Chemistry in the Drexel Institute, Philadelphia, Pa. New York : Henry Holt & Co. 1898.

The author has aimed, in this book, to make the matter

" as concise as possible with the least sacrifice of a study of reactions and solubilities of chemical importance," and for this reason " many of the reactions found in larger books have been omitted." The matter is arranged in groups, each one being taken up in turn, the characteristic precipitates discussed in order, and methods given for the separation of the members of the group and of the groups from one another. There is no new feature in the book, as it is only one of the many arrangements of the same material made by various teachers to serve their special needs. J. E. G.

EXPLOSIVE MATERIALS; THE PHENOMENA AND THEORIES OF EXPLOSION AND THE CLASSIFICATION, CONSTITUTION, AND PREPARATION OF EXPLOSIVES. By CAPTAIN J. P. WISSER, 7th Artillery. Instructor, Department of Military Science, United States Artillery School. New York : D. Van Nostrand Co. 1898. 16mo. 50 cents.

The first edition of this work appeared fifteen years ago, and the present edition has been entirely rewritten and brought up to date. For a general résumé of the nature and causes of explosions, the chemical composition of the explosives, the nature of the chemical acts involved, and the composition of all known explosives this book will serve as a handy reference. It is well written and attractive and contains a well arranged index and references to the larger works on this subject. It is one of the numbers of the Van Nostrand Science Series, and is sufficiently small to be carried in the pocket. J. E. G.

ELEMENTS OF GENERAL CHEMISTRY WITH EXPERIMENTS. By JOHN H. LONG, M.S., Sc.D., Professor of Chemistry and Director of the Chemical Laboratories in the Schools of Medicine and Pharmacy of Northwestern University. Chicago : E. H. Colegrove. 1898.

The author has prepared an excellent book which can be recommended as a valuable guide for elementary classes in chemistry. The matter is well arranged and the descriptive part is clear and not filled with unnecessary details. It is intended as a classroom and laboratory guide, the statements made being verified wherever possible by experiments for which explicit directions are given. The author has avoided the mistake so often made of plunging the student at once into a consideration of theories which cannot be understood without a groundwork of experimental results, and he has treated the atomic theory from an historical point of view. The book is well printed and bound, and attractive in every way. J. E. G.

A TEXT-BOOK OF ELEMENTARY ANALYTICAL CHEMISTRY, QUALITATIVE AND VOLUMETRIC. By JOHN H. LONG, M.S., Sc.D., Professor of Chemistry and Director of the Chemical Laboratories in the Schools of Medicine and Pharmacy of Northwestern University. Chicago: E. H. Colegrove. 1898. Price, $1.50.

This book is intended principally for the use of students of

medicine and pharmacy. The part devoted to qualitative analysis contains, beside the matter usually presented in such courses, methods for the detection of some common organic substances and poisons. The second part of the work is devoted to volumetric analyses as the author thinks that more knowledge can be gained, in the same length of time, by these methods than from the study of gravimetric ones. The general principles of volumetric analysis, the method of preparing the solutions, analyses by neutralization, precipitation and oxidation, the determination of sugar and related substances, the volumetric methods used in water analysis and the use of the nitrometer are considered in this part. This course, which is mapped out, should give the student a good general knowledge of the methods of volumetric analyses; but if, as in many of the medical schools is no doubt the case, the course in chemistry is not pursued any further, it would perhaps be more satisfactory to omit a part of this course and substitute a few typical cases of gravimetric methods.   J. E. G.

A LABORATORY GUIDE IN QUALITATIVE CHEMICAL ANALYSIS. By H. L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. New York: John Wiley & Sons; and London: Chapman & Hall. 1898.

This volume, of 154 pages, adds another to the many already existing manuals of qualitative inorganic analysis for use by beginners. Most of the facts and directions based upon them are of course substantially the same as those to be found in numerous other books having the same object in view.

A point deserving praise is the detailed study required from the experimenter of the exact behavior of given solutions with reagents, observing the effects of varying dilution, temperature, etc.

On the other hand, there is some ground for adverse criticism in the instructions with respect to " chemical equations", to which a separate chapter is devoted.

Such an expression as the following: " Thus, $Ag + Cl' = AgCl$, shows that solutions of any silver salt and any chloride when mixed (in neutral or acid solution) give a precipitate of silver chloride", is not only open to objection as too sweeping a statement in point of fact, but is liable to suggest to the beginner the too common idea that the formula found in the text-book is the *cause* of the phenomenon observed in the test-glass. The list is a very restricted one of the substances examined and the reactions used for their detection.   J. W. M

A SHORT COURSE IN INORGANIC QUALITATIVE ANALYSIS. For Engineering Students. By J. S. C. WELLS, Ph.D., Instructor in Analytical Chemistry, Columbia University. New York: John Wiley & Sons; and London: Chapman & Hall. 1898.

In the main the remarks made as to the work last noticed

apply also to this one. It is evidently intended for use by the author's pupils, and much oral explanation would be necessary to make it practically available, so that it can hardly be regarded as an independent treatise. For example, on p. 267, the student is told that in making a preliminary examination of the material before him he should "heat a portion gently with oxidizing flame upon charcoal." No doubt a blowpipe flame is meant, but nothing has been said about the blowpipe or what an oxidizing flame is. Lack of accuracy and clearness in the language used is likely to puzzle a beginner. Thus, on p. 9, having given as an example of an equation

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl.$$
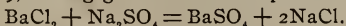
the author says : * * * * * * * *
" This brings us to another important property of symbols, *viz.*, that they not only represent the elements themselves, but they also represent their atomic weights, as compared with the atom of hydrogen which is taken as the unit." How the tyro is to find the atomic weights of the elements referred to in the equations from the symbols given is not easy to see. And, on p. 12, in reference to the equation

$$2FeCl_2 + Cl_2 = Fe_2Cl_6$$
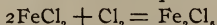
it is remarked : "Although oxygen does not enter into the reaction, we say that $FeCl_2$ has been oxidized." Such sentences are not likely to help the student along.

Sydney Smith is reported to have said of a man, who in a moment of impatience at a long-winded account of Arctic exploration had "damned the North Pole," that he had also gone so far as to " speak disrespectfully of the Equator." One is sometimes sorely tempted to use strong language in regard to *Equations*, in view of the misuse too often made of them in connection with chemical teaching.

In neither of the two books just noticed does reference seem to be made to a small stumbling block which students of analytical chemistry need to be guarded against ; namely, that arising from the almost universal presence in materials examined of " traces" of foreign substances in a state of accidental mixture. It is clearly desirable that work be not restricted to laboratory products in a condition of so-called purity, but that natural minerals, industrial products, etc., be also examined, and in these traces of non-essential iron, sodium, chlorine, etc., will frequently present themselves, making it needful that the student be taught how to judge *for himself* as to such traces, neither neglecting them altogether nor considering them as necessary constituents of the materials analyzed. J. W. M.

OBITUARY NOTICES.

J. A. R. NEWLANDS, whose name is so well known to chemists on account of the important part he played in the development of the Periodic System, died in England, July 29, 1898, at the age of sixty. In a book published by Mr. Newlands in 1884, all the papers published by the author on the question of the periodic arrangement of the elements were reprinted and his claim to priority in the matter defended. The first paper on the subject appeared in the *Chemical News* of Feb. 7, 1863, and was followed at short intervals by others on the same subject. Owing to the confusion prevalent then as to the correct atomic weights and to inconsistencies and inaccuracies in the arrangement, the "Law of Octaves" did not receive the attention it merited, and it was not until the papers of Mendeléeff and Lothar Meyer appeared that the great importance of the Periodic Law was realized. Mr. Newland's claim as the originator of the idea has, however, been generally recognized, and in 1887 he was awarded the Davy Medal of the Royal Society, in recognition of his work on the Periodic Law of Elements. Mr. Newlands did very little work in the field of pure chemistry, but devoted himself to the industrial side of the subject and especially to the sugar industry.

<div align="right">J. E. G.</div>

In the death of the Right Hon. Lord PLAYFAIR, K.C.B., F.R.S., which occurred May 29, 1898, the Chemical Society of England lost one of its oldest and most prominent members and an ex-president. He was 79 years old and had always taken a great interest in scientific questions. When 19 years old he went to Giessen and studied under Liebig and was appointed professor of chemistry in the Royal Institute at Manchester in 1843. After serving on a number of commissions appointed for the study of important sanitary measures for the kingdom, he was appointed professor of chemistry at the University of Edinburgh. He also served on several Royal Commissions, occupied the office of Postmaster-General, and held important offices in the House of Commons. The honors and titles to which he attained were marks of the appreciation in which he was held by the people for the beneficial results of the application of his wide and thorough scientific knowledge to questions of paramount importance to the nation.   J. E. G.

AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XIV.—CAMPHORIC ACID.

FIFTH PAPER.

By WILLIAM A. NOYES.

Synthesis of the Neighboring Xylic Acid.

In my last paper,[1] experiments of Mr. E. B. Harris and myself were described which led to the preparation of a ketone, by simple reactions, from cis-campholytic acid (the isolauronolic acid of Koenigs and Hoerlin[2]). The oxime of this ketone melted at 104°.[3] By an error in our thermometer we were led to think that the melting-point of this oxime approaches closely to that of the oxime of dimethyl-(1,3)-cyclohexanone(2) as given by Kipping,[4] and the identity of the

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[1] This JOURNAL, 18, 685.

[2] Ber. d. chem. Ges., 26, 814; 27, 3467; This JOURNAL, 17, 429.

[3] The melting-point is given in our paper as 112°-113°. The determination was made with an Anschütz thermometer graduated in fifths of a degree and supposed to be very accurate. In using it later I was led to question its accuracy, and on testing it found, to my surprise, that its record was 8°.5 too high at the boiling-point of water, and 5° too high at the boiling-point of glacial acetic acid. The melting-point of the oxime of the ketone derived from cis-campholytic acid was, therefore, 104°, instead of 112°-113°, as given. That of the oxime of dimethyl-(1,3)-cyclohexanone(2) was 115°-117° instead of 120°-122°, as given in our paper.

The melting-point of α-bromdihydro-cis-campholytic acid shou' also be 124°-125° instead of 129°-130°, as given in the same paper (This JOURNAL, 18, 689). The other six thermometers of the set were found, on testing, to be remarkably accurate and the other melting-points and boiling-points of the paper are correct.

[4] J. Chem. Soc., 67, 357 (1895).

two seemed possible. Both Kipping[1] and Zelinsky[2] have since given the melting-point of the pure oxime as 118°–119° aud the agreement in melting-points is now known to be illusory. Since, however, Zelinsky[3] gave the melting-point of the oxime at first as 104°–105°, and since both he and Kipping[4] have obtained evidence of a stereomeric form melting at a much lower temperature, it is still quite possible that the oxime of the ketone from cis-campholytic acid is a mixture of stereomers and that the ketone is in reality dimethyl-(1,3)-cyclohexanone (2). In any case it has seemed worth while to obtain positive evidence on the point by the synthesis of the Δ^1-tetrahydroxylic acid, C_6H_7 —$\begin{cases} CH_3 \ (1) \\ CO_2H \ (2) \\ CH_3 \ (3) \end{cases}$, and a comparison of its properties with those of cis-campholytic acid. The tetrahydro acid has not yet been obtained but the synthesis of the corresponding xylic acid has been effected and the remaining steps of the synthesis are reasonably certain. As it will be some time, however, before the work can be completed it seems desirable to give an account now of the portion already finished.

The neighboring xylic acid was obtained by Jacobsen[5] some years ago by melting the sodium salt of the 2-sulphonic acid of metaxylene with sodium formate. It is evident from the properties of the acid to be described in this paper that Jacobsen's acid was quite impure. He obtained it in very small amount and gives no analysis. His method of preparation appears so unpromising that no attempt to use it has been made.

Nitrile of the Neighboring Xylic Acid.

This nitrile appears to have been obtained, also, in impure condition by Jacobsen.[6]

I have prepared[7] the nitrile from the 2-aminometaxylene by Sandmeyer's reaction. The necessary xylidine was first

[1] Chem. News, **75**, 44. [2] Ber. d. chem. Ges., **30**, 1543.
[3] Ber. d. chem. Ges., **28**, 781. [4] *Loc. cit.*
[5] Ber. d. chem. Ges., **11**, 21. [6] *Loc. cit.*
[7] A portion of this work was done by Mr. W. E. Burk. See This JOURNAL, **18**, 692.

obtained by nitrating metaxylene,[1] reducing the dinitroxylenes with alcoholic ammonium sulphide, separating the two nitroxylidines with warm gasoline or ligroïn, eliminating the amino group and reducing the 2-nitroxylene with tin and hydrochloric acid. After separation of the two nitroxylidines by means of gasoline the purification of the 2-nitroxylidine is best effected by crystallization of its chloride, which is moderately soluble in pure water but quite difficultly soluble in hydrochloric acid.

The yield of 2-nitroxylidine was poor and other workers seem to have had the same experience. Our work leads us to think that a rapid nitration of small quantities of xylene at a low temperature would give better results than when the product is left longer in contact with nitrosulphuric acid. An attempt to prepare the 2-nitroxylene by the method of Miolati and Lotti[2] from diaminonitroxylene was not successful, probably because the abstracts[3] of their paper do not give sufficiently full details for practical use.

It was found, later, that the easiest method of obtaining the 2-xylidine in small amounts is from commercial xylidine. The samples which we have examined contain approximately 2 per cent. of the compound. 600 grams of the commercial xylidine were mixed with 150 cc. of glacial acetic[4] acid and the mixture was allowed to stand several hours to cool and crystallize. The crystals were sucked as dry as possible, and then washed with ligroïn till nearly white. These crystals are suitable for the preparation of pure asymmetric acetxylide (see below). The first filtrate and the xylidine recovered from the washings were washed with a strong solution of sodium hydroxide to remove acetic acid. It was then converted into the neutral sulphate by treatment with the calculated amount of dilute sulphuric acid. From the more soluble portions of the sulphates[5] 100 grams of xylidine were obtained. To this were added 13 grams of xylidine recovered after the preparation of pure asymmetric acetxylide as described

[1] Grevingk : Ber. d. chem. Ges., **17**, 2423.   [2] Gaz. chim. Ital., **27**, I, 293–99.

[3] Centralblatt, 1897, I, 1123 ; J. Chem. Soc., **72**, 560.

[4] Linebach : Ber. d. chem. Ges., **20**, 871.

[5] Nölting and Pick : Ber. d. chem. Ges., **21**, 3150.

below. The whole was mixed with 200 cc. of glacial acetic acid and boiled at such a rate that three-fourths of the acid distilled away in three hours. On fractioning the remainder, 34 grams of xylidine, boiling at 200°–250°, were obtained from the portion boiling below 300°. This was converted into acetxylide by means of acetic anhydride. On boiling the acetxylide obtained with four times its weight of 25 per cent. sulphuric acid for an hour there crystallized from the solution, on cooling, 12.6 grams of the neighboring acetxylide. This melted at 176°–176°.5, and was practically pure. A small additional amount may be recovered from the mother-liquors. In another case 1150 grams of the xylidine gave 23 grams of the acetxylide, melting at 178°–179°.

The acetxylide was saponified by boiling 20 grams of it with 30 cc. of concentrated sulphuric acid and 16 cc. of water for three hours.

The nitrile was prepared from the xylidine by Sandmeyer's reaction, as usual, using the diazo compound prepared in a solution in hydrochloric acid. In the earlier experiments the attempt was made to saponify the liquid which distilled with water vapor without further purification. Boiling for several days with alcoholic potash[1] appeared to convert it partly into the amide, but, after crystallization, treatment of the product with concentrated sulphuric acid and sodium nitrite[2] gave an acid the composition of which, on analysis, did not agree with that of xylic acid. After several ineffectual attempts to prepare the xylic acid by other methods the nitrile was again prepared and it was found that by fractioning the oil at first obtained it could be separated into two portions. The lower-boiling portion contained a considerable amount of chlorxylene. The higher-boiling portion solidified on cooling and was crystallized from ligroïn. This proved to be the pure nitrile.

The *nitrile* crystallizes from ligroïn in white prisms or thick needles. These are easily soluble in warm ligroïn, difficultly soluble in cold. It is easily soluble in alcohol and ether. It sublimes easily. The crystals melt at 89°.

[1] V. Meyer: Ber. d. chem. Ges., **29**, 834.
[2] Bouveault : Bull. Soc. Chim., **9**, 368.

0.1082 gram of the nitrile gave 11.85 cc. of nitrogen at a temperature of 25°.5 and a pressure of 647 mm.

	Calculated for $C_6H_9-CN\underset{CH_3}{\overset{CH_3}{<}}$	Found.
N	10.69	10.71

It is probable that the nitrile could be saponified by the method of Bouveault[1] as modified by Sudborough,[2] but, as the corresponding xylic acid has been prepared by another method, no further experiments to that end have been tried.

Attempts to Prepare Hexahydroxylic Acid from Dimethylcyclohexanone.

An attempt was next made to prepare hexahydroxylic acid from dimethyl-(1,3)-cyclohexanone-(2). The necessary dimethylpimelic acid, $CH_2\begin{cases}CH_2CH<\overset{CH_3}{CO_2H}\\CH_2CH<\overset{CH_3}{CO_2H}\end{cases}$, was prepared,[3] partly by the method sketched in my last paper,[4] partly by using methylmalonic ester and trimethylene bromide, partly from methyl acetacetic ester and trimethylene bromide.[5] The trimethylene bromide was prepared from trimethylene glycol, partly by means of phosphorus tribromide, partly by mixing it with concentrated hydrobromic acid and distilling slowly, separating the aqueous portion of the distillate from the trimethylene bromide formed and distilling the former again. This latter method proved more satisfactory.

The dimethylpentanetetracarboxylic acid which was obtained as an intermediate product is spoken of in the literature[6] as easily soluble in water. I have found it quite difficultly soluble in cold water, and that it may be easily purified by crystallization from hot water. The pure acid melts

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[1] *Loc. cit.* [2] J. Chem. Soc., **67**, 601.

[3] I wish here to express my sincere thanks to Professor A. A. Noyes, who very kindly furnished me with 200 grams of trimethyleneglycol, obtained by fractioning an impure glycerin, for use in preparing the necessary trimethylene bromide. See J. Am. Chem. Soc., **17**, 890.

[4] This JOURNAL, **18**, 694; Perkin : J. Chem. Soc., **51**, 241; Perkin and Prentice : *Ibid*, **59**, 823, 829.

[5] Kipping and Mackenzie : *Ibid*, **59**, 577; Kipping : Chem. News, **74**, 279.

[6] Perkin and Prentice : *Loc. cit.* The melting-point is there given as 200°–205°.

with decomposition at 210°–211°, when heated quickly. The acid was analyzed as follows :

0.2451 gram of the acid gave 0.1288 gram H_2O, and 0.4264 gram CO_2.

	Calculated for $CH_2<^{CH_2-C<^{CH_3}_{(CO_2H)_2}}_{CH_2-C<^{(CO_2H)_2}_{CH_3}}$		Found.
C_{11}	132	47.83	47.44
H_{16}	16	5.80	5.84
O_8	128	46.37	....

Dimethylcyclohexanone was prepared from the dimethyl-pimelic acid by distilling with an excess of lime.

From the ketone an attempt was, at first, made to prepare and saponify the cyanhydrine. This proving unsuccessful, another portion of the ketone was reduced to dimethylcyclo-hexanol by means of moist ether and sodium,[1] and from the alcohol the bromide was prepared by warming with concentrated hydrobromic acid in a sealed tube.[2] The bromide was boiled for two hours with potassium cyanide in alcoholic solution (80 per cent.) and the resulting cyanide was boiled with alcoholic potash (33 per cent.) for some time. No evidence of the formation of more than mere traces of the desired hexa-hydroxylic acid could be obtained. It is quite possible that by the use of larger quantities of material, and by a careful study of the conditions, one or both of these methods could be made successful, but the difficulties are so great that the method was abandoned.

Attempts to Prepare Derivatives of Xylic Acid from Ethylidene-diacetacetic Ester.

Some time ago Knoevenagel[3] obtained ethylidenediacet-acetic ester,

$$CH_3-CO-CH-CO_2C_2H_5$$
$$CH_3-CH$$
$$CH_3-CO-CH-CO_2C_2H_5$$
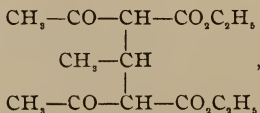
[1] Baeyer: Ann. Chem. (Liebig), **278**, 106. [2] *Loc. cit.*, p. 107.
[3] *Ibid*, **281**, 104.

by condensing acetacetic ester with acetaldehyde at a low temperature by use of a small amount of piperidine or diethylamine. When ethylidenediacetacetic ester is heated to 140°–150° for three or four hours with twice its weight of water in a sealed tube, it condenses to a cyclic compound, and loses carbon dioxide and ethyl alcohol. In his first paper[1] Knoevenagel considered that a mixture of two bodies,
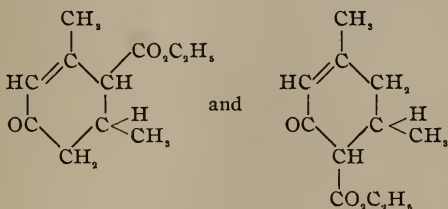
of which the second was soluble in a cold dilute solution of sodium hydroxide, is formed by this treatment. In a recent paper,[2] owing to Callenbach's[3] work with similar compounds, he considers it more probable that the mixture consists of a mixture of the ketone and "enol" forms of the second compound. I have, of course, only studied the matter so far as was necessary for the purpose in view, but my work has incidentally proved that the mixture contains the ketone form (or at least a form insoluble in cold dilute sodium hydroxide) of the δ-ketone ester. It has also rendered it probable that the β-ketone ester is present, and I consider it altogether likely that both ketone and "enol" forms of both bodies are formed.

Before the complex nature of the mixture was understood, several attempts were made to reduce the portion insoluble in a cold dilute solution of sodium hydroxide, in the hope of obtaining the corresponding hydroxy-hexahydroxylic acid. Analyses of the products formed demonstrated that a partial reduction was effected, but, as no definite compounds were isolated, further details are unnecessary.

[1] *Loc. cit.*, p. 110.   [2] Ann. Chem. (Liebig), **297**, 144.
[3] Ber. d. chem. Ges., **30**, 639.

Next the mixture was converted into derivatives of benzene by methods similar to that by which Knoevenagel converted 3,5-dimethyl-Δ^2-cyclohexenone[1] into the symmetric xylenol.

A mixture of 6.7 grams of the ester, distilled under diminished pressure[2] with 15 cc. of chloroform, was cooled to 0° and a mixture of 1.8 cc. (1 molecule) of bromine with 10 cc. of chloroform was slowly added. In the course of ten or fifteen minutes the bromine was decolorized without appreciable evolution of hydrobromic acid. After about two hours the chloroform was distilled away and the residue heated for from five to ten minutes on the water-bath. The last portions of the chloroform were removed by evacuating the distilling-bulb while still hot. On treating the cold residue with ether, there remained undissolved about 0.6 gram of a white solid which was found, after crystallization from alcohol, to consist of the aromatic hydroxy acid corresponding to the δ-ketone ester.

Dimethyl-(1,3)-phenol-5-methylic-(2) acid as thus obtained is a white powder, difficultly soluble in ether, chloroform, and water, more easily soluble in alcohol. It gives only a slight yellow color with ferric chloride. These properties demonstrate that the carboxyl group is in position (2) and not (4). The acid melts at 253°–254°.

0.1098 gram of the acid gave 0.0607 gram H_2O, and 0.2627 gram CO_2.

	Calculated for $C_6H_2\begin{smallmatrix}CH_3\\CO_2H\\CH_3\\OH\end{smallmatrix}$.		Found.
C_9	108	65.06	65.25
H_{10}	10	6.02	6.13
O_3	48	28.92	....
	166		

The ethyl ester of dimethyl-(1,3)-phenol-5-methylic acid was found to be present in the ethereal mother-liquors mentioned above, and was purified by crystallization, partly from chloro-

[1] Ann. Chem. (Liebig), **281**, 121.

[2] Experiments with the portion of the distilled ester which was insoluble in cold dilute sodium hydroxide gave practically the same results as when the distilled ester was used directly. It would seem that in this, as in so many other cases, the ketone and "enol" forms pass readily, one into the other.

form, partly from alcohol. It crystallizes from alcohol in plates, from water in needles. It melts at 98°. It gives a yellow color with ferric chloride in alcoholic solution. It is soluble in a solution of sodium hydroxide and precipitated again by carbon dioxide. The ester could not be saponified by long boiling with alcoholic potash, with an aqueous solution of sodium hydroxide, or with hydrobromic acid.

0.1641 gram of the ester gave 0.1071 gram H_2O, and 0.4070 gram CO_2.

	Calculated for C_6H_2 $\begin{cases} CH_3 \\ CO_2C_2H_5 \\ CH_3 \\ OH \end{cases}$		Found.
C_{11}	132	68.04	67.64
H_{14}	14	7.21	7.25
O_3	48	....	....
	194		

Although the amount of the hydroxy acid obtained was small, an attempt was made to reduce it with absolute alcohol and sodium, by the method used by Einhorn and Coblitz[1] for *m*-hydroxybenzoic acid.

A portion of the original acid was recovered unchanged, a considerable portion was converted into a compound soluble in sodium hydroxide and reprecipitated by carbon dioxide, and only a very small amount was converted into an acid more easily soluble in ether than the original acid, and which may have contained some of the hexahydroxy acid desired. The method was evidently hopeless and was abandoned.

Attempts to Prepare Xylic Acid by Means of Acetobromxylene and Acetoiodoxylene.

In accordance with the experiments of Schöpff[2] and of Claus,[3] it would seem that when halogen derivatives of benzene are treated with aluminium chloride and acetyl chloride the acetyl group enters in a position para to the halogen when that position is free. Since, further, the acetyl group is readily introduced into mesitylene and the symmetric

[1] Ann. Chem. (Liebig), **291**, 299.   [2] Ber. d. chem. Ges., **24**, 3766.
[3] J. prakt. Chem. [2], **44**, 355.

durene, it would seem probable that a similar treatment of the symmetric bromxylene or iodoxylene would give a compound with the acetyl group ortho to the two methyl groups. From such compounds the neighboring xylic acid could be easily obtained by oxidation and elimination of bromine.

The asymmetric acetxylide required was prepared by boiling the xylidine acetate referred to in the earlier part of this paper with an equal weight of glacial acetic acid for four or five hours, allowing the acetic acid to distil very slowly. 600 grams of the commercial xylidine gave 272 grams of the crude acetate, and this gave 164 grams of the pure acetxylide after one crystallization from strong alcohol and 16 grams were obtained from the mother-liquors.

Bromxylene was, at first, prepared by the direct bromination of acetxylide, saponification of the bromacetxylide, by boiling with concentrated hydrochloric acid and elimination of the amino group. The bromination was effected partly in solution in glacial acetic acid, with or without the addition of iron, partly in solution in chloroform. In the latter case 19 grams of acetxylide, 50 cc. of chloroform, 50 cc. of water, and 6 cc. (18.6 grams) of bromine were shaken together in a glass-stoppered bottle for half an hour. After saponification with concentrated hydrochloric acid, and separation from dibromxylidine as directed by Genz,[1] the bromxylidine was distilled with water vapor and crystallized from ligroïn. In this way the pure bromxylidine of Genz, melting at 96°–97°, was obtained. The yield was poor, and there was a considerable amount of a compound easily soluble in ligroïn, probably an isomer, formed.

An attempt was at first made to eliminate the amino group by dropping a hydrochloric acid solution of the hydrazine compound into a boiling solution of copper sulphate in accordance with the directions given by Erdmann[1] for metachlorparatoluidine. Instead of the desired bromxylene, chlorbromxylene was formed in considerable amount. A subsequent study of the literature bearing on the case makes it seem that Erdmann's directions are seriously at fault.

[1] Ber. d. chem. Ges., 3, 225.
[2] Anleit. z. Darstellung org. chem. Präparate, p. 71.

4-chlor-2-brommetaxylene,[1] prepared as indicated, crystallizes from alcohol in pearly white leaflets, which melt at 68°. It boils at 244°. It is moderately soluble in alcohol and is slowly volatile with water vapor.

I. 0.1941 gram gave 0.2900 gram AgCl + AgBr, and 0.1876 gram Ag.

II. 0.2509 gram gave 0.3748 gram AgCl + AgBr and 0.2439 gram Ag.

	Calculated for $C_6H_2\underset{\textstyle\diagdown Br}{\overset{\textstyle\diagup (CH_3)_2}{\text{—Cl}}}$.	Found.	
		I.	II.
Cl + Br	52.60	52.59	52.17

In later experiments the amino group of the bromxylidine was eliminated, partly by use of ethyl nitrite and absolute alcohol, partly by treatment of the alkaline diazo solution with an alkaline solution of stannous chloride.[2]

By dissolving the resulting bromxylene in carbon bisulphide, adding aluminium chloride and acetyl chloride and boiling for a short time, then decomposing with water, as usual, an acetobromxylene was obtained which boiled at 275°-278° and solidified in a freezing-mixture. After spreading on porous porcelain and washing with a little ligroïn it melted at 33°. Since the symmetric bromxylene prepared from the symmetric xylidine (see below) gives an acetobromxylene which does not solidify in a freezing-mixture, even on adding a crystal of this compound, and since the asymmetric brommetaxylene gives us no acetyl derivative[3] when treated with aluminium chloride and acetyl chloride, it would seem that the bromxylene obtained from this bromxylidine must be the 2-brommetaxylene. Wroblewski,[4] however, obtained, by treatment of this bromxylene with ethyl bromide and sodium, an ethyldimethylbenzene, which gave, by oxidation, a very small amount of mesitylenic acid and a larger amount of uvitic acid. It would seem from his results, therefore, that this bromxylene is the symmetric form.

[1] For the probable position of the bromine atom see below.

[2] Merz and Effront: Ber. d. chem. Ges., **17**, 2329; Culmann and Gasiorowski: J. prakt. Chem. [2], **40**, 97; R. Friedländer: Ber. d. chem. Ges.. **22**, 587.

[3] Schöpff: Ber. d. chem. Ges., **24**, 3769.   [4] Ann. Chem. (Liebig), **190**, 215.

The evidence here presented is not altogether satisfactory, and it would not be at all difficult to obtain more positive proof for the position of the groups, but I have not been able to find time to follow the matter further.[1]

Preparation of Symmetric Xylidine.

The symmetric bromxylene next used was prepared from the symmetric xylidine by Sandmeyer's reaction. As I have found the directions given in the literature for the nitration of the asymmetric acetxylide very unsatisfactory,[2] it seems worth while to give the methods which were finally used.

25 grams of acetxylide were dissolved in 50 cc. of warm glacial acetic acid and the solution cooled to about 40°. 10 cc. of a mixture of 15 cc. concentrated sulphuric acid and 25 cc. nitric acid (sp. gr. 1.42) were added and the remainder of the mixture was added in portions of 5 cc. at a time at intervals of ten minutes. The temperature must be watched closely, and if it begins to rise rapidly the flask must be cooled as vigorously as possible under the tap. In several cases the temperature rose, in spite of vigorous cooling, to 80°–90° without serious effect upon the yield. After all of the acid has been added and the mixture has stood for from ten to twenty minutes, the whole was poured into about 300 cc. of water. After filtering and washing, the moist product was saponified by boiling in a tightly covered beaker, for from two to three hours, with 135 cc. of concentrated, commercial hydrochloric acid. After filtering, on a hardened filter, from a small amount of tar, the 5-nitroxylidine was precipitated by the addition of 3 or 4 volumes of water. The 6-nitroxylidine present remains in solution. After filtering and washing, the 5-nitroxylidine may be separated from the water which it contains by melting it in a small covered porcelain dish on the water-bath and allowing it to cool. 98 grams of acetxylide nitrated in this manner, in four portions, gave 69 grams of 5-nitroxylidine.

To eliminate the amino group, 25 grams of the nitroxyli-

[1] Since writing the above I find that Vaubel (Ztschr. anal. Chem., **36**, 286) states that on brominating asymmetric acetxylide the bromine enters in position 2 or 6.

[2] Nölting and Forel : Ber. d. chem. Ges., **18**, 2677.

dine were dissolved in a mixture of 125 cc. of absolute alcohol and 30 cc. of concentrated sulphuric acid, the mixture was cooled quickly to 0°, and, as soon as possible, to avoid crystallization, the ethyl nitrite generated from 25 grams of sodium nitrite[1] and dried in gaseous form by passing over calcium chloride, was passed into the mixture. After a short time the mixture was heated slowly to boiling and boiled for a few minutes till decomposition was complete. A considerable amount of water was then added and the nitroxylene was distilled with a current of steam. The nitroxylene was warmed on the water-bath for some time with a strong solution of sodium hydroxide to saponify any ethoxynitroxylene formed,[2] and, after cooling and washing, the nitroxylene was crystallized from alcohol. 69 grams of the 5-nitroxylidine gave 39 grams of 5-nitroxylene. This was reduced by warming it on the water-bath for two or three hours, with an upright condenser, after adding 50 grams of powdered iron, 100 cc. of water, and 30 cc. of acetic acid (30 per cent.). After adding an excess of sodium hydroxide and distilling with steam, 28 grams of the symmetric xylidine were obtained.

The xylidine was converted into 5-bromxylene by Sandmeyer's reaction, as usual. The yield was poor.

To prepare the acetobromxylene, 5 grams of the bromxylene, 25 cc. of carbon bisulphide, 5 grams of aluminium chloride, and 5 cc. of acetyl chloride were mixed and boiled with a reversed condenser for three-quarters of an hour. After decomposing with dilute hydrochloric acid and fractioning twice, 3.25 grams of acetobromxylene boiling at 272°–276° were obtained.

*4-Aceto-5-brom-*1,3-*xylene* is an oil which does not solidify in a freezing-mixture.

0.1315 gram gave 0.1075 gram AgBr.
0.1225 gram gave 0.1015 gram AgBr.

	Calculated for $C_6H_2{<}{(CH_3)_2 \atop COCH_3} \atop Br$	Found.	
		I.	II.
Br	35.24	34.84	35.14

[1] Wallach and Otto: Ann. Chem. (Liebig), **253**, 251.
[2] Nölting and Forel: Ber. d. chem. Ges., **18**, 2678.

When bromacetoxylene is oxidized with a warm alkaline solution of potassium permanganate, *bromxylylglyoxalic acid*,

$$C_6H_2 \underset{Br}{\overset{(CH_3)_2}{\diagup}} COCO_2H,$$
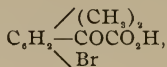
is formed. After filtering and acidifying, this separated as an oil and was not further studied. If dilute sulphuric acid is added to the hot solution, without filtering off the oxides of manganese, the glyoxalic acid is oxidized to bromxylic acid. The reaction seems to be general and appears to be a very satisfactory means of obtaining acids from acetyl derivatives of benzene.

Bromxylic acid, $C_6H_2 \begin{cases} CH_3 & (1) \\ CH_3 & (3) \\ CO_2H & (4) \\ Br & (5) \end{cases}$, crystallizes from alcohol
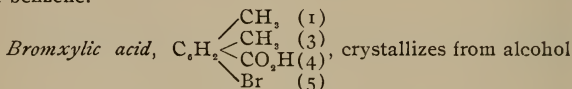
in long, very fine needles, which melt at 183°–184°. On warming for a short time with zinc dust and ammonia, the bromine is easily removed. The resulting acid was distilled with water vapor and then melted at 126°. It was, therefore,

the asymmetric xylic acid, $C_6H_3 \begin{cases} CH_3 & (1) \\ CH_3 & (3) \\ CO_2H & (4) \end{cases}$, and this estab-

lishes the constitution of the compounds described, as given.

0.1166 gram of acid gave 0.0951 gram AgBr.

	Calculated for $C_6H_2 \underset{Br}{\overset{(CH_3)_2}{\diagup}} CO_2H.$	Found.
Br	34.94	34.71

Since the yield in the preparation of the symmetric bromxylene was poor, experiments were also undertaken with the symmetric iodoxylene. The latter was prepared by pouring a diazo solution prepared from the symmetric xylidine, in dilute hydrochloric acid, into an excess of a concentrated solution of potassium iodide, and warming till the decomposition was complete.

Symmetric iodoxylene is an oil which boils at 117° under a pressure of 27 mm. and at 234°–235° under atmospheric pressure.

Acetoiodoxylene, $C_6H_2 \underset{\overset{\displaystyle \diagdown}{I}}{\overset{\diagup CH_3 \quad (1)}{\underset{\diagdown COCH_3(4)}{\overset{\displaystyle - CH_3 \quad (3)}{}}}}$ $\begin{matrix}(5)\end{matrix}$, was prepared by mixing

13.3 grams of iodoxylene with 55 cc. of carbon bisulphide, adding 11 grams of aluminium chloride and then, carefully, 9 cc. of acetyl chloride. The mixture was boiled for half an hour on the water-bath, with reversed condenser, and was then treated with cold dilute hydrochloric acid, as usual. After distilling under diminished pressure 10.8 grams of acetoiodoxylene and 1.85 grams of recovered iodoxylene were obtained. The ketone boils at 171° under a pressure of 25 mm. and at 295°-298°, with some decomposition, under atmospheric pressure. During the boiling of the mixture with aluminium chloride there was some liberation of iodine, and it would seem, from the results of the oxidation, that there was a partial change in the position of the iodine atom. The ketone did not solidify in a freezing-mixture.

0.1528 gram of the ketone gave 0.1319 gram AgI.
0.1379 gram of the ketone gave 0.1186 gram AgI.

	Calculated for $C_6H_2 \underset{\diagdown I}{\overset{\diagup (CH_3)_2}{- COCH_3}}.$	Found.	
		I.	II.
I	46.35	46.64	46.45

If the ketone is oxidized in an ice-cold alkaline solution of potassium permanganate with constant agitation, *iodoxylyl-glyoxalic acid*, $C_6H_2 \underset{\diagdown I}{\overset{\diagup (CH_3)_2}{- COCO_2H}}$, is formed. After filtering and

adding an acid this is precipitated as an oil.

The *barium salt*, $\left(C_6H_2 \underset{\diagdown I}{\overset{\diagup (CH_3)_2}{- COCO_2}} \right)_2 Ba + 2\tfrac{1}{2}H_2O$, crystallizes

on cooling its hot solution. It is quite difficultly soluble even in hot water.

	Calculated.	Found.			
		I.	II.	III.	IV.
$2\tfrac{1}{2}H_2O$	5.71	5.54	6.07	5.45	5.35

	Calculated for anhydrous salt.	Found.		
		I.	II.	III.
Ba	18.48	18.50	18.06	17.98

If the iodoxylylglyoxalic acid is oxidized by means of manganese dioxide and sulphuric acid, it gives the corresponding iodoxylic acid. This was also obtained, mixed with a bibasic acid, by shaking the ketone, at ordinary temperatures, with an alkaline solution of potassium permanganate, and, after the reduction of the latter was complete, heating on the water-bath and adding dilute sulphuric acid. The mixture of acids obtained was separated by conversion into the barium salts. The salt of the bibasic acid separated on cooling the concentrated solution and was easily purified by recrystallization.

Iodomethylterephthalic acid, $C_6H_2 \begin{cases} CH_3 \ (1) \\ CO_2H (2) \\ I \qquad (5) \\ CO_2H (3) \end{cases}$, obtained from

this barium salt, crystallizes from hot water in fine, short needles, which melt at 298°. When the acid was treated with zinc dust and ammonia it gave a difficultly soluble acid which melted at 328°–330° (corr.). The only authorities which I can find[1] give the melting-point of methylterephthalic acid, (α-xylidinic acid), as 280°–283°. It was supposed at first, therefore, that the acid obtained must be methylisophthalic acid,[2] which melts at 320°–330°. To make sure, methylterephthalic acid was

prepared by oxidizing xylic acid, $C_6H_3 \begin{cases} CH_3 \ (1) \\ CH_3 \ (3) \\ CO_2H (4) \end{cases}$ (m.p. 126°)

with an alkaline solution of potassium permanganate. The acid at first precipitated from the filtered solution melted at about 280°, but by dissolving the acid in ammonia and precipitating the hot, dilute solution with hydrochloric acid and repeating the operation several times, the melting-point rose to 325°–330°. Finally the calcium salt was prepared. This is only moderately soluble in water. The air-dried salt lost 18.58 per cent. of water at 138°, and the anhydrous salt gave 18.05 per cent. Ca. Theory, 18.35 per cent. The acid separated from the calcium salt melted with decomposition at 330°–335°. When zinc chloride was added to the solution of the calcium salt no precipitate was formed but a copious pre-

[1] Fittig and Laubinger : Ann. Chem. (Liebig), **151**, 276; Remsen and Iles : This JOURNAL, **i**, 120.

[2] Claus : J. prakt. Chem. [2], **42**, 509.

cipitate separated on warming and redissolved on cooling. It seems certain, therefore, that pure methylterephthalic acid melts at about 330° and not at 280°-283°, as former observers have stated.

The *barium salt*, $C_6H_2 \begin{cases} CO_2 \\ CO_2 \\ CH_3 \\ I \end{cases} > Ba + 6H_2O$, is moderately

soluble in cold water, easily soluble in hot. The salt effloresces easily.

	Calculated.	I.	II.	III.	IV.
			Found.		
$6H_2O$	19.66	18.81	18.79	19.39	19.43

I. 0.1986 gram of the anhydrous salt gave 0.1051 gram $BaSO_4$.

II. 0.1976 gram of the salt gave 0.1040 gram $BaSO_4$.

	Calculated.	Found.	
		I.	II.
Ba	31.35	31.15	30.95

The filtrate from the barium salt contained two iodoxylic acids. The copper salt of one of these was precipitated on adding a solution of copper nitrate. The acid was recovered by shaking the salt with dilute hydrochloric acid and ether, and was crystallized from alcohol for analysis.

Iodoxylic acid, $C_6H_2 \begin{cases} CH_3 & (1) \\ CH_3 & (3) \\ CO_2H & (4) \\ I & (5)(?) \end{cases}$, crystallizes from alcohol in

small granular crystals, which melt at 196°–197°. It is practically insoluble in cold water and very difficultly soluble in hot water. When warmed with zinc dust and ammonia it gave xylic acid, which, after distilling with water vapor, melted at 126°.

0.1310 gram of the acid gave 0.1111 gram AgI.

	Calculated.	Found.
I	45.97	45.80

The *barium salt* is very easily soluble in water.

The *copper salt*, $\left(C_6H_2 \begin{matrix} (CH_3)_2 \\ CO_2 \\ I \end{matrix} \right)_2 Cu + nH_2O$ is very diffi-

cultly soluble in water. It contained variable amounts of
water (5.28 and 7.57 per cent. in two determinations). The
salt was analyzed by dissolving it in alcohol with the addi-
tion of some hydrochloric acid, precipitating the copper with
hydrogen sulphide and washing the cupric sulphide with
alcohol.

0.2240 gram of the dry salt gave 0.0281 gram Cu_2S.
0.3453 gram of the dry salt gave 0.0455 gram Cu_2S.

	Calculated.	Found. I.	II.
Cu	10.36	10.02	10.49

On adding hydrochloric acid to the filtrate from this copper
salt a second iodoxylic acid was precipitated. From this a
barium salt was prepared and from the crystallized barium
salt the acid was again obtained and crystallized from hot
water. The acid then melted at 172°–173°. The acid is
much more easily soluble in hot water than its isomer. After
reduction with zinc dust and ammonia it gave xylic acid
melting at 126°. It is evident, therefore, that both iodoxylic
acids are derived from the same xylic acid. The iodine is
probably ortho to the carboxyl in one and meta in the other.
The ortho acid could probably be distinguished by the prepa-
ration of an iodoso[1] compound from it, but experiments for
that purpose have not been undertaken.

$$\text{The } \textit{barium salt, } \left(C_6H_2 \overset{\diagup(CH_3)_2}{\underset{\diagdown I}{-CO_2}} \right)_2 Ba + 6H_2O, \text{ crystallizes}$$

from the concentrated solution in needles which are easily
soluble in water.

0.1005 gram of the salt lost 0.0133 gram H_2O at 140°, and
gave 0.0297 gram $BaSO_4$.

	Calculated.	Found.
$6H_2O$	13.58	13.23
Ba	17.39	17.37

Preparation of the Neighboring Xylic Acid from Acetomesitylene.

The work which has just been described having demon-
strated that the acetyl groups of bromacetoxylene and of iodo-

[1] V. Meyer: Ber. d. chem. Ges., **28**, 83; V. Meyer and Kloeppel: *Ibid*, **26**, 1733.

acetoxylene are not in the desired position, experiments were next undertaken with acetomesitylene. These have led to the synthesis of the neighboring xylic acid by means of the following series:

The mesitylene was prepared by the method of Orndorff and Young,[1] slightly modified. As the yield was considerably greater than is reported by others, it seems worth while to give the details. 180 grams of acetone (228 cc.) were placed in a liter distilling-bulb and cooled in ice-water or in a freezing-mixture of ice and commercial hydrochloric acid, 300 grams of concentrated, commercial sulphuric acid (165 cc.) were run in with constant agitation and as rapidly as possible without allowing the temperature to rise above 20°. After sixteen to twenty hours the mixture was heated slowly over a low flame at such a rate that the reaction began in fifteen to twenty minutes. After the reaction had continued for two or three minutes the flame was removed and a moderately rapid current of steam passed in. After three to four minutes longer the receiver was changed and the portions coming over later collected in a separate flask. The distillation with steam was continued till about 200 cc. had passed over. After distilling four portions in this way the oil coming

over in the second part of the distillations was separated from the aqueous portion of the distillate and was distilled again with water vapor. This effects a partial separation of the mesitylene from high-boiling oils which interfere seriously if the mixed oils are fractioned directly. After 600–800 cc. of the distillate have been collected the residue in the distilling-bulb may be discarded as worthless. The oil which passed over with the steam was mixed with the oil which came over in the first part of the first distillation, washed with a solution of sodium hydroxide, dried with calcium chloride, and fractioned once, with a Ladenburg distilling-bulb, before treatment with sodium. The portion boiling from 150°–210° was collected in 5 portions. The fractionation was then repeated twice with the addition of metallic sodium. In this way 720 grams of the acetone gave 81 grams of mesitylene boiling at 163°–167°, and 4.5 grams 167°–170°. This makes 17.2 per cent. of the theory, while Orndorff and Young[1] obtained 11.5 per cent. of pure mesitylene, and Lucas[2] recently obtained only 13 per cent. (45 grams from 500 grams of acetone) boiling from 160°–170°.

Acetomesitylene was prepared by the method of V. Meyer and Molz.[3] The pure compound boils at 240°–241° with an Anschütz thermometer. Claus[4] gives 235° (uncorr.).

Claus has described[5] an acid which he supposed to be 2,6-dimethylterephthalic acid and which he obtained by oxidizing 2,4,6-trimethylbenzoic acid with potassium permanganate. Jannasch and Weiler[6] have also obtained the 2,6-dimethylterephthalic acid. They obtained it, along with other products, by heating 1,2,3,5-tetramethylbenzene with dilute nitric acid in a sealed tube. I have prepared the acid by the oxidation of acetomesitylene, with the intermediate formation of 2,4,6-trimethylbenzoic acid. At the same time about one-half of the compound is oxidized to the 4,6-dimethylphthalic acid. The properties of the dimethyltere-phthalic acid which I have obtained agree with those ascribed

[1] *Loc. cit.* [2] Ber. d. chem. Ges., **29**, 953.
[3] Ber. d. chem. Ges., **30**, 1271. [4] J. prakt. Chem. [2], **41**, 504.
[5] J. prakt. Chem. [2], **41**, 507. [6] Ber. d. chem. Ges., **28**, 534.

to the acid of Jannasch and Weiler, but cannot be reconciled with the statement of Claus.

Oxidation of Acetomesitylene.

10 grams of the acetomesitylene were put in a 500 cc. glass-stoppered bottle with 3 grams of sodium hydroxide and 25–30 cc. of water. 20 grams of potassium permanganate were dissolved in 200 cc. of hot water. About 30 cc. of the solution were cooled and added to the contents of the bottle containing the acetomesitylene. The stopper was inserted and the whole was shaken vigorously. The remainder of the permanganate was added in portions of 30–40 cc. at intervals of about five minutes, the vigorous shaking being continued after each addition. The bottle was occasionally cooled so far that the temperature did not rise above 40°–45°. After all of the permanganate had been added and the mixture had been shaken for a short time longer, the contents of the bottle were transferred to a liter flask and heated on the water-bath till the reduction of the permanganate was complete. The solution now contained, chiefly, mesitylglyoxalic acid, $C_6H_2{<}^{(CH_3)_3}_{COCO_2H}$. 50 cc. of dilute sulphuric acid (25 per cent.) were then added, carefully, with shaking, and the heating was continued for a short time. This causes the oxidation of the mesitylglyoxalic acid to trimethylbenzoic acid. The solution was then cooled, 16 grams of sodium hydroxide were added, and then a solution of 25.6 grams of potassium permanganate in 250 cc. of water was added in two portions at an interval of thirty to sixty minutes. The amount of permanganate used is that calculated for the oxidation of the trimethylbenzoic acid to a bibasic acid and also for the oxidation of the manganese sulphate, formed during the oxidation of the mesitylglyoxalic acid, to manganese dioxide. After two to three hours, or longer, the solution was again warmed on the water-bath till the reduction of the permanganate was complete. 150 cc. of dilute sulphuric acid were then carefully added and, after warming for a short time longer, a strong solution of acid sodium sulphite was added till the oxides of

manganese passed into solution. Most of the dimethyltere-
phthalic acid remains undissolved. A small additional
amount separates on cooling. The acid was filtered off,
washed, dissolved in ammonia, filtered from a small amount
of an indifferent body which is formed, precipitated again
with sulphuric acid, and thoroughly washed on a Witts' plate
with the pump. 10 grams of the acetomesitylene gave 5
grams of the acid.

2,6-Dimethylterephthalic acid separates, on precipitation, as
a very voluminous, amorphous precipitate. It is very diffi-
cultly soluble in hot or cold water and is also difficultly solu-
ble in ether. It is easily soluble in alcohol, less soluble in
alcohol containing hydrochloric acid.

1,3-Dimethyl-4,5-dimethylic Acid.

About one-half of the acetomesitylene appears to be oxi-
dized to dimethylphthalic acid. This separates from the
mother-liquors above, on concentration and cooling. The
acid has not been carefully studied, but it is, apparently,
moderately soluble in water, difficultly soluble in ether.
When heated above its melting-point it is converted into the
anhydride.

The *anhydride*, $C_6H_2 \underset{\diagdown(CH_3)_2}{\overset{\diagup CO}{-CO}}{>}O$, was purified by dissolving

in ether, shaking the ethereal solution with a solution of
sodium carbonate, and, after evaporation of the ether, crys-
tallizing from ligroïn. It crystallizes in fine white needles,
which melt at 116°.

0.1046 gram gave 0.0444 gram H_2O, and 0.2615 gram CO_2.

	Calculated for $C_6H_2\overset{\diagup CO}{\underset{\diagdown(CH_3)_2}{-CO}}{>}O$.		Found.
C_{10}	120	68.18	68.18
H_6	8	4.54	4.52
O_3	48	....	....
	176		

Acid Methyl Ester of 2,6-Dimethylterephthalic Acid.

Twenty-five grams of dimethylterephthalic acid were put in a flask with 125 cc. of methyl alcohol, and 4 grams of dry hydrochloric acid passed into the mixture. The whole was boiled with reversed condenser for about five hours. After distilling away most of the alcohol, as much as possible of the remainder was removed by evacuating the flask with the filter-pump, while the residue was shaken and gently warmed for a short time. The residue was then used for the preparation of the amide as described below. For analysis the ester was crystallized from water. It crystallizes from water in fine, woolly needles. It crystallizes from alcohol in somewhat coarser needles. It melts at 189°–190°.

0.1571 gram gave 0.0837 gram H_2O, and 0.2618 gram CO_2.

		Calculated for $C_6H_2\overset{\diagup(CH_3)_2}{\underset{\diagdown CO_2H}{-CO_2CH_3}}$.	Found.
C_{11}	132	63.46	62.81
H_{12}	12	5.77	5.92
O_4	64	....	....
	208		

According to V. Meyer's law of esterification,[1] the ester group must be in position 5 and not in position 2 with regard to the methyl groups.

To prepare the *amide* corresponding to the ester the residue referred to above was dissolved in 40 cc. of ammonia (10 per cent.), the solution extracted once with ether, and filtered, with care not to increase the volume, and most of the ether in the solution removed by careful exhaustion in a vacuum desiccator. The solution was then nearly saturated with ammonia gas and allowed to stand at summer temperature, 28°–30°, for two or three days. At the end of that time an amount of the ammonium salt of the amide corresponding to 30–40 per cent. of the weight of acid used had separated in crystalline form. This was filtered on a plate covered with asbestos, washed with a little ammonia, dissolved in water, and the pure amide precipitated by hydrochloric acid.

[1] Ber. d. chem. Ges., **27**, 510; **28**, 2773.

2,6-Dimethylterephthalamidic acid, C_6H_2
$\begin{matrix}\diagdown(CH_3)_2\\-CO_2H\\\diagdown CONH_2\end{matrix}$, crystal-

lizes from water in white needles which melt at 246°. The amide is easily saponified by boiling with a solution of sodium hydroxide and was analyzed in this way.

The distillate from 0.0621 gram of the amide required for neutralization 6.4 cc. of $\frac{1}{20}$-normal HCl.

	Calculated for $C_6H_2\begin{matrix}(CH_3)_2\\-CO_2H\\CONH_2\end{matrix}$	Found.
N	7.25	7.21

From the ammoniacal mother-liquors mentioned above the dimethylterephthalic acid may be recovered and, by repeating the esterification and treating with ammonia, a new portion can, of course, be converted into the amide.

2,6-Dimethyl-4-aminobenzoic Acid.

3.86 grams of the amide were rubbed thoroughly in a mortar with 45 cc. of an ice-cold solution of sodium hydroxide (10 per cent.). A cold solution of 3.2 grams (1.05 cc.) of bromine in 25 cc. of sodium hydroxide was added carefully with thorough cooling in ice-water. The solution was filtered from a little undissolved amide on an asbestos filter, and the filtrate warmed quickly to near the boiling-point in a water-bath. After cooling, 28 cc. of dilute hydrochloric acid (25 per cent.) were added, the solution was filtered and extracted twice with ether. On adding 15 grams of crystallized sodium acetate the amino acid separated slowly in pure crystalline condition. From the filtrate a small additional amount may be obtained by evaporating in a distilling-bulb under diminished pressure. Evaporation in an open dish causes a decomposition of the acid.

2,6-Dimethyl-4-aminobenzoic acid, C_6H_2
$\begin{matrix}\diagup CO_2H\,(1)\\CH_3\,(2)\\\diagdown NH_2\,(4)\\CH_3\,(6)\end{matrix}$, crys-

tallizes slowly from water in needles which melt with decom-

position at 194°–195°. It is difficultly soluble in water, alcohol, or ether. The *chloride* is also difficultly soluble. When the solution in hydrochloric acid is evaporated to dryness on the water-bath, the acid is almost completely decomposed with the formation of symmetric xylidine. The xylidine was identified by means of its acetyl derivative, melting at 139°.[1] The acetyl derivative prepared from the symmetric xylidine described in the earlier part of this paper melted at exactly the same temperature.

Neighboring Xylic Acid.

From the amino acid, 2,6-dimethyl-4-iodobenzoic acid was prepared by the method given by Wachter[2] for the preparation of *o*-iodobenzoic acid from anthranilic acid. The acid was dissolved in ammonia (10 per cent.), zinc dust added, and the solution warmed for some time on the water-bath. The solution was filtered, acidified, and extracted with ether. The residue left on distilling the ether was distilled with water vapor, the distillate extracted with ether, and the residue from the ethereal solution crystallized from ligroïn.

The *neighboring xylic acid*, $C_6H_3 \begin{cases} CH_3 & (1) \\ -CO_2H & (2) \\ CH_3 & (3) \end{cases}$, crystallizes

from ligroïn in white needles which melt at 116°.[3] The acid is more easily soluble in water than its isomers. It is slowly volatile with water vapor, but very little of the acid separates from the distillate. It is very easily soluble in ether, rather difficultly soluble in cold ligroïn.

0.1752 gram of the acid gave 0.1062 gram H_2O and 0.4623 gram CO_2.

		Calculated for $C_6H_3 \begin{smallmatrix} CH_3 \\ -CO_2H \\ CH_3 \end{smallmatrix}$.	Found.
C_9	108	72.00	71.70
H_{10}	10	6.67	6.73
O_2	32	....	....
	150		

[1] The melting-point is variously given. Wroblewski: Ann. Chem. (Liebig), **207**, 96, gives 144°.5; Thöl: Ber. d. chem. Ges., **18**, 362, gives 138°; Nölting and Forel: *Ibid*, **18**, 2678, give 140°.5.

[2] Ber. d. chem. Ges., **26**, 1744.

[3] Jacobsen gives the melting-point as 97°-99°. Ber. d. chem. Ges., **11**, 21.

The preparation of this xylic acid leaves the main point for which this investigation was undertaken still untouched. Now that a method for its preparation has been discovered, however, it is hoped that the remainder of the work will soon be completed.

ON SOME RELATIONS AMONG THE HYDRATES OF THE METALLIC NITRATES.

BY J. H. KASTLE.

It is a remarkable fact that by far the greater number of the hydrates of the metallic nitrates contain either 3, 4, 6, 9, or 12 molecules of water, and that in by far the greater number of these salts the number of molecules of water is some simple multiple of three (3). This relation has already been commented upon by other observers. In seeking for some explanation of this relation, it occurred to the writer that these hydrates are to be regarded as addition-products of the base and one of the hypothetical nitric acids;[1] and in this connection it is to be noted that Armstrong[2] in 1891, and again in 1895, in discussing the formation of salts, stated it as probable that the acid and base first unite, and that the salt is formed by an intramolecular change in the addition-product thus produced. There are certainly a great many hydrates of salts known, whose composition is exactly the sum of the acid and the base from which they are derived. The following are a few common examples of hydrates of this type: $CaSO_4.2H_2O$; $BaCl_2.2H_2O$; $HgNO_3.H_2O$, etc. In applying this consideration to the hydrates of the metallic nitrates it is remarkable how simple the relations existing between these compounds appear. According to this supposition we have several different classes of nitrates, which may be regarded as distinct salts of the several hypothetical nitric acids: H_5NO_6, H_3NO_4, HNO_3, N_2O_5, etc.

To the first class belong all of the anhydrous nitrates.

[1] Other observers have found it necessary to assume the existence of salts of the hypothetical nitric acids. For example, in order to account for the lack of color of dilute aqueous solutions of ferric nitrate, Antony and Gigli [Gaz. chim. Ital., **26** (1), 293-311 (1896)] have assumed the existence, in such solutions, of the ferric salts of the acids $H_4N_2O_7$ and H_5NO_6.

[2] Proc. Chem. Soc., 1891, 118.

These compounds may be regarded as addition-products of the anhydride of nitric acid and the metallic oxide, and are probably derived as follows : $M'_2O + N_2O_5 = 2M'NO_3$.

The following anhydrous nitrates are known : KNO_3, $LiNO_3$, $NaNO_3$, $RbNO_3$, $CsNO_3$, $AgNO_3$, $Pb(NO_3)_2$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Mg(NO_3)_2$, $TlNO_3$, $Ga(NO_3)_3$, $KAu(NO_3)_4$, $RbAu(NO_3)_4$, $KAu(NO_3)_4$, $KAg(NO_3)_2$, $RbAg(NO_3)_2$.

The second class includes a few nitrates which are probably to be regarded as addition-products of ordinary nitric acid and the metallic base, thus : $M(OH) + HNO_3 = MNO_3.H_2O$. Only a few examples of this class are known. These are the following : $HgNO_3.H_2O$, and $Th(NO_3)_4.4H_2O$.

The third class consists of a considerable number of nitrates of the bivalent and trivalent metals whose composition is identical with that of addition-products of ortho-nitric acid, H_3NO_4, and the metallic base. These salts may be looked upon as deriving as follows :

(1) $M^{II}(OH)_2 + 2H_3NO_4 = M^{II}(NO_3)_2.4H_2O$.

(2) $M^{III}(OH)_3 + 3H_3NO_4 = M^{III}(NO_3)_3.6H_2O$.
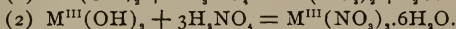
The following compounds are to be included in this class :

$Cd(NO_3)_2.4H_2O$,	$Di(NO_3)_3.6H_2O$,
$Ca(NO_3)_2.4H_2O$,	$Fe(NO_3)_3.6H_2O$,
$Sr(NO_3)_2.4H_2O$.	$Tl(NO_3)_3.6H_2O$,
	$Ce(NO_3)_3.6H_2O$,
	$Er(NO_3)_3.6H_2O$,
	$La(NO_3)_3.6H_2O$,
	$Sm(NO_3)_3.6H_2O$,
	$Y(NO_3)_3.6H_2O$.
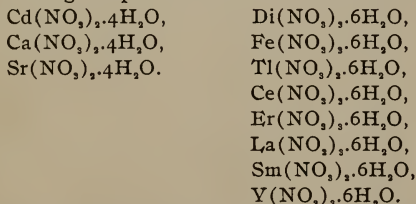
A number of double nitrates containing very large amounts of water of crystallization would seem also to belong to this class :

$2Ce(NO_3)_3.3CO(NO_3)_2.24H_2O$,
$2Ce(NO_3)_3.3Mg(NO_3)_2.24H_2O$,
$2Ce(NO_3)_3.3Mn(NO_3)_2.24H_2O$,
$2Ce(NO_3)_3.3Ni(NO_3)_2.24H_2O$,
$2Ce(NO_3)_3.3Zn(NO_3)_2.24H_2O$,
$2La(NO_3)_3.3Mg(NO_3)_2.24H_2O$,
$2La(NO_3)_3.3Mn(NO_3)_2.24H_2O$,
$2La(NO_3)_3.3Ni(NO_3)_2.24H_2O$.
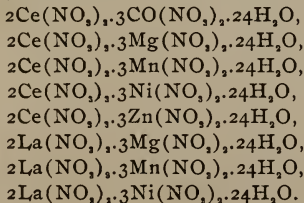
These double nitrates may be regarded as deriving, as follows :

$$2M^{III}(OH)_3.3M^{II}(OH)_2 + 12H_3NO_4 = 2M^{III}(NO_3)_3.$$
$$3M^{II}(NO_3)_2.24H_2O.$$
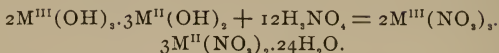
The fourth class also includes a large number of nitrates of the bivalent and trivalent metals whose composition is that of an addition-product of the acid, H_6NO_6, and the metallic base. These compounds are to be looked upon as deriving as follows :

$$M^{II}(OH)_2 + 2H_6NO_6 = M^{II}(NO_3)_2.6H_2O,$$
$$M^{III}(OH)_3 + 3H_6NO_6 = M^{III}(NO_3)_3.9H_2O,$$
$$M^{IV}(OH)_4 + 4H_6NO_6 = M^{IV}(NO_3)_4.12H_2O.$$
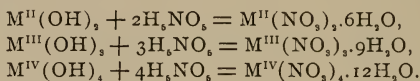
Among the bivalent metals we find the following members of this class of hydrates: $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_2.6H_2O$, $Mg(NO_3)_2.6H_2O$, $Mn(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$, $Ca(NO_3)_2.6H_2O$.

Among the trivalent metals we find the following: $Al(NO_3)_3.9H_2O$, $Cr(NO_3)_3.9H_2O$, $Fe(NO_3)_3.9H_2O$.

A double nitrate of didymium and nickel is also to be included in this class. This salt has the composition $2Di(NO_3)_3.3Ni(NO_3)_2.36H_2O$, and probably derives as follows : $2Di(OH)_3 + 3Ni(OH)_2 + 12H_6NO_6 = 2Di(NO_3)_3.$ $3Ni(NO_3)_2.36H_2O.$

The most remarkable example of this class of compounds, however, is furnished by the metal thorium. This metal combines with four nitric acid groups, and its ordinary hydrate contains 12 molecules of water of crystallization, $Th(NO_3)_4.12H_2O$. It is to be regarded, therefore, as deriving as follows : $Th(OH)_4 + 4H_6NO_6 = Th(NO_3)_4.12H_2O$.

A fifth class includes a few nitrates which may be regarded as deriving from pyronitric acid, $H_4N_2O_7$, by the direct addition of the metallic base, thus : $M^{II}(OH)_2 + H_4N_2O_7 = M^{II}(NO_3)_2.3H_2O$. To this class belong the following : $Cu(NO_3)_2.3H_2O$, $Ge(NO_3)_2.3H_2O$, $Mn(NO_3)_2.3H_2O$.

Similarly, the octohydrate of thallium nitrate, $Tl(NO_3)_3.$ $8H_2O$, probably derived from the acid, $H_{12}N_3O_{14}$, thus : $Tl(OH)_3 + H_{12}N_3O_{14} = Tl(NO_3)_3.8H_2O$. The acid, $H_{12}N_3O_{14}$,

may be regarded as $3H_6NO_6$—H_2O. Altogether about 70 normal nitrates are described in the literature, and of this number 53 are included in these 5 classes of compounds, and hence come under the rule laid down concerning their composition; *viz.*, that they are to be regarded as addition-products of one of the hypothetical nitric acids and their respective bases. Among these seventy nitrates several are included whose composition is as yet considered doubtful, such as rhodium and zirconium nitrates, $Rb(NO_3)_3.2H_2O(?)$ and $Zr(NO_3)_4.5H_2O(?)$. But even including a number of such doubtful cases, it is certain that 75 per cent. of all the normal metallic nitrates now known conform to the rule under discussion. It can scarcely be doubted, therefore, that these suppositions respecting the composition of this important class of salts contain at least some element of truth.

The many basic nitrates which are known at present have not been included in this discussion, but even these become more intelligible in the light of this hypothesis. Pattison Muir[1] has already pointed out that certain basic nitrates, such as one of the basic lead nitrates, may be regarded as salts of the hypothetical orthonitric acid, H_3NO_4; thus $HPbNO_4$ and $Pb_3(NO_4)_2$ are both known. So, in the same way, if we disabuse our minds of the older notions regarding water of crystallization, the thought suggests itself with reference to the hydrates of the normal nitrates that they are in reality acid salts of complex acids, corresponding in some respects to chlorplatinic acid, and similar compounds, and in such compounds as $Fe(NO_3)_3.9H_2O$ or $H_{18}FeN_3O_{18}$ and $Cu(NO_3)_2.3H_2O$ or $H_6CuN_2O_9$, etc., etc., it is easy to conceive of a further replacement of hydrogen by the metal, and hence, of the formation of so-called basic salts. A few examples, selected somewhat at random from the many basic nitrates described in the literature, are sufficient to indicate that the composition of these salts can be explained by the same general considerations that have already been applied to the interpretation of the normal nitrates. The relation of several of these basic salts to the hypothetical nitric acids is indicated in the following table :

[1] Watts' Dictionary of Chemistry; Muir and Morley, Vol. III, 509.

Old formulas of basic nitrates.	New formulas of basic nitrates.	Acids of basic nitrates.
1. $Fe_2N_2O_8$	$2FeNO_4$	$H_8N_2O_8 = 2H_4NO_4$
2. $Mg_3N_2O_8$	$Mg_3(NO_4)_2$	$H_8N_2O_8 = 2H_4NO_4$
3. $2Hg'_2O.N_2O_5.H_2O$	$H_2Hg'_4N_2O_8$	$H_8N_2O_8 = 2H_4NO_4$
4. $2ZnO.N_2O_5.3H_2O$	$H_6Zn_2N_2O_{10}$	$H_{10}N_2O_{10} = 2H_5NO_5$
5. $2Hg''O.N_2O_5.3H_2O$	$H_6Hg''_2N_2O_{10}$	$H_{10}N_2O_{10} = 2H_5NO_5$
6. $3MnO.N_2O_5.3H_2O$	$H_4Mn_3N_2O_{10}$	$H_{10}N_2O_{10} = 2H_5NO_5$
7. $Bi_2O_3.N_2O_5.2H_2O$	$H_4Bi_2N_2O_{10}$	$H_{10}N_2O_{10} = 2H_5NO_5$
8. $10PbO.3N_2O_5.5H_2O$	$H_{10}Pb_{10}N_6O_{30}$	$H_{36}N_6O_{30} = 6H_5NO_5$
9. $Ca(NO_3)_2.Ca(OH)_2.H_2O$	$H_4Ca_2N_2O_9$	$H_8N_2O_9 = (2H_5NO_5 - H_2O)$
10. $4ZnO.N_2O_5.2H_2O$	$H_2Zn_4N_2O_{11}$	$H_{12}N_2O_{11} = (2H_5NO_5 + H_2O)$
11. $2Fe_2O_3.N_2O_5.2H_2O$	$H_4Fe_4N_2O_{12}$	$H_{16}N_2O_{12} = (2H_5NO_5 + 3H_2O)$
12. $8NiO.2N_2O_5.5H_2O$	$H_{10}Ni_8N_4O_{22}$	$H_{28}N_4O_{22} = (4H_5NO_5 + 3H_2O)$
13. $5NiO.N_2O_5.4H_2O$	$H_8Ni_5N_2O_{14}$	$H_{16}N_2O_{14} = (2H_5NO_5 + 4H_2O)$

The relation of these basic salts to the nitric acids is clearly shown in the above table, and requires no further comment, except to say that it is almost inconceivable that the really fundamental relations existing between these salts could be indicated by means of the formulas usually employed in representing their composition, and which are given in the first column of the table. Compounds 2 and 3 in the table, for example, are both salts of the same acid; *viz.*, H_4NO_4, a fact which is certainly not indicated by a direct comparison of the formulas usually assigned them; and the same may be said of compounds 6 and 7, both of which are salts of H_5NO_5. The fact that in the case of compounds 10, 11, 12, and 13 we are forced to represent their respective acids as hydrates of the acid H_5NO_5 would seem to indicate that the valence of nitrogen towards hydrogen and oxygen is even greater than 5. Indeed the necessity for such an assumption would also seem to exist even among certain hydrates of the normal nitrates. For example, the composition of the double nitrate of cobalt and didymium, $2Di(NO_3)_3.3CO(NO_3)_2.48H_2O$, can only be explained according to these suppositions by assuming it to be a salt of the monohydrate of the acid H_5NO_5. On such an assumption its formation might be accounted for in this way: $2Di(OH)_3.3Co(OH)_2 + 12H_5NO_5.H_2O = 2Di(NO_3)_3.-3CO(NO_3)_2.48H_2O$. In such a compound as $H_5NO_5.H_2O$ the nitrogen atom is probably septavalent.

There are only two hydrates that are more complex than those already mentioned. These are the double nitrates, $2La(NO_3)_3.3M(NO_3)_2.69H_2O$ and $2Di(NO_3)_3.3M(NO_3)_2.69H_2O$, which were obtained by Frerichs and Smith[1] in 1876. These hydrates are so complex that exceedingly careful analytical work will be required to determine their composition, and so many revisions of atomic weights have been made since these compounds were investigated that even the theoretical percentage of their components is open to correction. For the present, therefore, these two cases will not be considered.

In conclusion it may be said that, while our knowledge concerning the nature and relations of hydrates is still most unsatisfactory, it is certain that many chemists are coming to believe in the atomic constitution of such compounds just as thoroughly as they admit such a constitution for hydrochloric acid, ammonia, marsh gas, and all the simpler chemical compounds. There are also not a few who are coming to believe that the valence hypothesis in its present shape will have to be modified, perhaps fundamentally, in order to make it applicable to many well-known chemical species which at present it is not sufficient to explain.

In view of these conditions, it is believed that the considerations above advanced are to be regarded as a step in the right direction; and it is the intention of the writer to further develop these and similar ideas when the opportunity presents itself. Certain classes of salts, such as the chlorates, bromates, etc., exhibit many close analogies in composition to the metallic nitrates, and in all likelihood a similar explanation will be found to hold good for the hydrates of these several classes of salts.

State College of Kentucky,
Lexington, Sept., 1898.

[1] Ann. Chem. (Liebig), **191**, 346–359.

LIQUID AMMONIA AS A SOLVENT.

By E. C. Franklin and C. A. Kraus.

The properties of liquid ammonia as a solvent were made the subject of investigation by G. Gore in the year 1872. In the account of his work, which appeared in the Proceedings of the Royal Society, Gore gives a list of about 350 substances upon which experiments were made. "The investigation was made for the purpose of ascertaining the general solvent properties of liquid ammonia, and to detect any manifest chemical actions between it and the various substances."[1] The tests were made in Faraday tubes, in which the ammonia, generated by heating dry ammoniochloride of calcium, was condensed upon the substance to be studied contained in the second arm of the tube, by refrigeration and its own pressure. The substances examined were for the most part inorganic bodies, including elementary substances and metallic salts, together with a few organic compounds. The results obtained, as stated in an abstract[2] in the Proceedings, are as follows: "The only elements soluble were the alkali metals, also iodine, sulphur, and phosphorus. (Bromine not tried.) The more frequently soluble salts were the nitrates, chlorides, bromides, and iodides. While oxides, fluorides, carbonates, sulphides, and sulphates were generally insoluble. Many saline substances, especially certain chlorides, bromides, iodides, and sulphates absorbed ammonia freely and swelled up greatly but did not dissolve. The behavior of the chlorides of mercury was peculiar. Various compounds of carbon were submitted to the action of the solution of potassium in liquid ammonia, the free potassium disappeared, but no elementary carbon was liberated."

Previous to the work of Gore, Weyl[3] and Seeley[4] had also investigated the action of liquid ammonia on a number of substances. They both, however, gave their attention especially to the blue solution formed by the solution of metallic sodium and metallic potassium in liquid ammonia.

[1] Proc. Roy. Soc., **21**, 140 (1873).   [2] *Ibid*, **20**, 441 (1872).

[3] Pogg. Ann., **121**, 601 and 697 (1863); **123**, 350 (1864).

[4] Chem. News, **23**, 169 (1871); Jour. Frank. Inst., **91**, 110 (1871).

These solutions Weyl believed to contain sodammonium, NH_3Na, and potassammonium, NH_3K, or an alloy of the metals with ammonium, NH_4, while Seeley considered them to be simple solutions of the metals in ammonia.

Joannis[1] followed up the study of these sodium and potassium solutions. He investigated the action of a number of substances on sodium and potassium in solution in liquid ammonia, and further, by means of vapor-tension and boiling-point measurements, determined the molecular formulae of the compounds in solution to be $N_2H_6Na_2$ and $N_2H_6K_2$, or $NaH_3N—NH_3Na$ and $KH_3N—NH_3K$, respectively.[2]

The authors in their turn have taken up the study of liquid ammonia with reference to its power as a solvent, and as they have been relieved, by the commercial manufacturers of liquid ammonia, of the necessity of preparing their solvent by the tedious method of Faraday, they have been able to study the behavior of liquid ammonia toward some 500 different substances under much more favorable conditions than were possible at the time Gore carried on his investigations. The results of this work are given below.

Method of Making the Tests.

The ammonia used in these experiments was the ordinary commercial article, such as is furnished by the manufacturers to ice-making plants. For the purpose of carrying out the tests, a quantity of ammonia was drawn from the steel stock cylinder into a medium-sized Dewar test-tube, from which the liquid was removed in quantity to suit the experiment in hand. The transfer of the liquid to the smaller tube in which the test was to be made was easily accomplished by means of a small pipette. The substance to be tested was introduced into this tube, in small quantity at a time and, in case the substance was a solid, in the form of fine powder, and its behavior in contact with the ammonia noted. As nearly as possible the attempt has been made to estimate the solubilities and to express them in accordance with the plan made use of by the editors of the last edition of Watts' Dictionary

[1] Compt. rend., **109**, 900 and 965 (1890) ; **112**, 337 and 392 (1891) ; **113**, 795 (1892) ; **114**, 585 (1892) ; **116**, 1370 and 1518 (1893) ; **118**, 713 and 1149 (1894) ; **119**, 557 (1895).

[2] *Ibid*, **115**, 820 (1893).

of Chemistry. Whether a salt, which from simple inspection appeared to be insoluble, was entirely insoluble or not, was determined by making a measurement of the conductivity of the solution. Those salts indicated in the tables as very slightly soluble formed solutions possessed of distinct conductivity. Salts which produced but a very slight increase in the conductivity of the ammonia are indicated as insoluble. No claim for great accuracy in the estimation of the solubilities of the various salts and more especially of the organic substances can be made, but we believe that in general they are fairly accurate.

General Results.

We have investigated the solubilities of 175 salts, some of which had previously been examined by Gore[1] together with 250 carbon compounds.

Elements.—Of the elements Gore reports the alkali metals, lithium, sodium, potassium, and rubidium, and the non-metals iodine, sulphur, and phosphorus to be soluble in ammonia. Copper is slowly acted on by ammonia, especially in the presence of air. We find caesium and selenium to be soluble also.

Fluorides.—The fluorides are insoluble. Of the 15 fluorides tested by Gore but 3 are reported to be at all soluble.

Chlorides.—The chlorides of the alkali metals are but sparingly soluble, while the chlorides of some of the heavy metals are readily soluble. The chlorides of the alkaline earth metals are practically insoluble. The chlorides of magnesium, calcium, strontium, barium, zinc, cadmium, manganese, cobalt, nickel, and lead, when added to liquid ammonia are rapidly acted on by the solvent, considerable heat being generated, and the salts at the same time undergoing a sort of slaking process.[2] The compact particles of the salts swell up and disintegrate, forming a bulky mass, which, while generally insoluble in ammonia, often readily dissolves in an ammonia solution of ammonium nitrate. The substances thus formed are in all probability the already known addition-products of

[1] *Loc. cit.*   [2] Observed also by Gore, *loc. cit.*

the respective salts. That such a compound is formed by the action of liquid ammonia on anhydrous calcium chloride, is shown by the following ammonia determinations :

0.1893 gram substance dissolved in water gave on titration with standard acid solution 0.1002 gram, or 53.00 per cent. ammonia.

0.4735 gram substance lost on ignition, 0.2515 gram, or 53.12 per cent. ammonia.

The calculated amount of ammonia in the compound $CaCl_2.8NH_3$,[1] is 55.15 per cent.

Bromides.—Judging from the limited number of bromides available for our tests, the bromides are more readily soluble than the chlorides. They are in all respects similar to the chlorides in their behavior, except that they are somewhat more soluble.

Iodides.—Most of the iodides are very readily soluble. Of the salts tested with a solution of ammonium iodide,[2] only barium and strontium nitrates gave immediate precipitates, and in these cases the crystalline character of the precipitates showed that even these iodides are probably slightly soluble. The iodides of magnesium, zinc, and cadmium (the iodides of calcium, strontium, and barium were not tested) are disintegrated as are the corresponding chlorides and bromides. The products of the action are, however, much more soluble than the compounds formed from the other halides. The iodides of silver, mercury, and lead dissolve so rapidly that the slaking phenomenon is scarcely to be observed.

Sulphates.—The sulphates, including sulphuric acid and ammonium sulphate, are entirely insoluble. Neither can the smallest quantity of finely powdered ammonium sulphate be observed to go into solution, nor does the addition of a quantity of the sulphate of ammonium, sodium, potassium, lead, silver, or mercury, alter the high electrical resistance of the solvent.

Sulphides.—But few sulphides have been tested directly for their solubility. Ferrous sulphide and native lead, antimony

[1] Joannis [Compt. rend., **112**, 337 (1891)] has prepared the compound $BaCl_2.8NH_3$ by the action of liquid ammonia on anhydrous barium chloride.

[2] *Vide* article on "Metathetic Reactions" to appear in the January number of this JOURNAL.

and copper sulphides are insoluble. Ammonium sulphide and native arsenous sulphide are soluble.

Sulphites.—The sulphites are insoluble.

Carbonates.—The carbonates are insoluble.

Oxides and Hydroxides.—The oxides and hydroxides tested were found to be insoluble. Mercuric oxide dissolved readily in a solution of ammonium nitrate, as did also, but less readily, cobalt oxide.

Phosphates.—The orthophosphates, metaphosphates, and pyrophosphates examined were found to be insoluble. The hypophosphites are slightly soluble.

Oxalates.—Ammonium oxalate and oxalic acid are insoluble.

Arsenates.—The only arsenates tested, ammonium arsenate and copper arsenate, are insoluble.

Cyanides.—The cyanides are generally easily soluble.

Cyanates and Sulphocyanates.—These salts are, so far as tested, very easily soluble.

Ferrocyanides and Ferricyanides.—The potassium salts are insoluble.

Nitrates.—All the metallic nitrates tested, with the exception of the nitrate of bismuth, are readily soluble; and even this salt goes into solution on the addition of ammonium nitrate to the solvent.

Nitrites.—The three nitrites tested are very easily soluble.

Paraffin Hydrocarbons.—The paraffin hydrocarbons are very slightly soluble or insoluble. The only members of the group tested, *viz.*, hexane and diisoamyl are not perceptibly soluble.

Halogen Derivatives.—The halogen substitution-products of methane and ethane are all either miscible with ammonia or are readily soluble. Derivatives of the higher hydrocarbons are slightly soluble.

Alcohols.—The lower members of the series, up to and including octyl alcohol, are miscible. Cetyl alcohol is insoluble.

Ethers.—Diethyl ether is miscible. Diamyl ether is slightly soluble.

Polyhydroxy Alcohols.—Glycol and glycerin are miscible

with ammonia.   Erythrite, dulcite, and mannite are slightly soluble.

Aldehydes.—The simpler aldehydes and their derivatives are either miscible or easily soluble.

Acids.—The fatty acids and their halogen substitution-products are readily soluble; the solubility decreasing with the higher members of the series.   The fatty acids proper are not perceptibly soluble.

Dibasic Acids.—The dibasic acids are insoluble.

Ethereal Salts.—The ethereal salts are readily soluble. The members of the group with the lower molecular weights are miscible, the solubility diminishing with increasing molecular weight.

Compounds Containing Nitrogen.—The nitrils, cyanates, sulphocyanates, the amines, the amido acids, the acid amides and the ureides are generally readily soluble.   The secondary amines are less easily soluble than the primary amines, while the one tertiary amine tested, trimethylamine, is miscible.

Hydroxy Acids.—The hydroxymonobasic acids are readily soluble ; the hydroxydibasic acids are but slightly soluble.

Sugars.—The sugars are very easily soluble.   Cane-sugar in concentrated solution forms a thick syrup.

Aromatic Hydrocarbons.—At atmospheric pressure ammonia dissolves about 10 per cent. of its weight of benzene.   Toluene is slightly soluble ; the isomeric xylenes and ethylbenzene are much less soluble than toluene, while the higher members of the group are not perceptibly soluble.

Halogen Derivatives.—The halogen derivatives are slightly soluble.

Nitro Derivatives.—The nitro-derivatives are moderately soluble.

Amido Derivatives.—Aniline and the toluidines are very easily soluble.   The secondary and tertiary amines are slightly soluble.

Phenols.—The phenols are extremely soluble, as are also such ethers as were tested.

Substituted Phenols.—The nitrophenols and the amidophenols are very easily soluble.

Alcohols.—The two tested are miscible.

Aldehydes.—Such as were tested are very easily soluble.

Acids.—The aromatic monobasic acids are readily soluble.

Substituted Acids.—The halogen, hydroxy, nitro, and amido substitution-products are generally readily soluble.

Dibasic Acids.—The dibasic acids are insoluble.

Ethereal Salts.—The ethereal salts are soluble.

Sulphonic Acids.—Such salts and other derivatives of the sulphonic acids as were tested are soluble.

Acid Amides and Anilides.—Such of these compounds as were tested are readily soluble.

Naphthalene and Derivatives.—But few of the derivatives of naphthalene were tested. Naphthalene itself is slightly soluble. The naphthols and naphthylamines are soluble.

Pyridine and Quinoline.—Pyridine and quinoline are miscible. Isoquinoline is slightly soluble.

Terpenes.—The terpenes are insoluble.

TABLE OF SOLUBILITIES OF CERTAIN METALLIC SALTS AND ORGANIC SUBSTANCES IN LIQUID AMMONIA.

The degree of solubility is indicated by the following abbreviations: v. e. sol., very easily soluble; v. sol., very soluble; m. sol., moderately soluble; sl. sol., slightly soluble; v. sl. sol., very slightly soluble; insol., insoluble. Experiments made by Gore are indicated by (G). Tests made by Gore which have been repeated by us are marked (FK).

Ammonium Salts.

Ammonium arsenate,	insol.
" borate,	sl. sol.
" bromide,	v. sol.
" carbonate, (G)(FK)	insol.
" chloride, (G)(FK)	v. sol.
" chromate,	sl. sol.
" hypophosphite,	m. sol.
" iodide,	v. e. sol.
" molybdate	insol.
" nitrate, (G)(FK)	v. e. sol.
" oxalate,	insol.
" oxalurate,	m. sol.
" phosphate,	insol.
" selenate,	insol.
" sulphate,	insol.
" sulphide,	v. sol.
" sulphocyanate,	v. e. sol.

Ammonium thionurate,	m. sol.
" vanadate, (G)	insol.

Aluminium Salts.

Aluminium acetate,	insol.
" chloride	insol.
" metal, (G)	insol.

Antimony Salts.

Antimony potassium tartrate,	insol.
" metal, (G)	insol.
" bromide, (G)	v. sol.
" chloride, (G)	insol.
" fluoride, (G)	insol.
" iodide, (G)	action.
" oxide, Sb_2O_3, (G)	insol.
" oxybromide, (G)	sl. sol.
" oxychloride, (G)	insol.
" sulphide red, (G)	insol.

Antimony sulphide, orange,(G)insol.
"   " black,(G)(FK)insol.
"   fluoride, (G)   insol.

Arsenic Salts.

Arsenic metal, (G)(FK)   insol.
Arsenous oxide, (G)(FK)   insol.
Arsenic acid, cryst., (G)   v. sl. sol.
Arsenous chloride, (G)   action
"   iodide, (G)(FK)   action
Realgar, (G)   m. sol.
Orpiment, (G)(FK)   sl. sol.

Barium Salts.

Barium acetate,   v. sl. sol.
"   hydroxide,   insol.
"   metal, (G)   insol.
"   chloride, (G)(FK)   insol.
"   nitrate, (G)(FK)   m. sol.
"   oxide, (G)   insol.
"   sulphate, (G)(FK)   insol.

Bismuth Salts.

Bismuth iodide,   sl. sol.
"   oxychloride,   insol.
"   nitrate,   sol. on ad-
                              dition of ammonium nitrate
"   metal, (G)   insol.
"   carbonate, (G)   insol.
"   chloride, (G)   m. sol.
"   fluoride, (G)   insol.
"   hydroxide, (G)   insol.
"   sulphide, (G)   insol.

Boron Compounds.

Boron, (G)   insol.
Boric anhydride, (G)   insol.
"   acid,   sl. sol.

Cadmium Salts.

Cadmium iodide, (G) insol.,
                (FK)   sl. sol.
"   nitrate,   m. sol.
"   sulphate,   insol.
"   bromide, (G)(FK)   insol.
"   carbonate, (G)   insol.
"   chloride, (G)(FK)   insol.
"   fluoride, (G)   insol.
"   sulphide, (G)(FK)   insol.

Calcium Salts.

Calcium acetate,   v. sl. sol.
"   bromide,   sl. sol.
"   butyrate,   insol.
"   carbonate,   insol.
"   formate,   insol.
"   nitrate,   v. e. sol.

Calcium oxide,   insol.
"   phosphate,   insol.
"   sulphide,   insol.
"   sulphite,   insol.
"   metal, (G)   white coating formed.
"   chloride, (G)(FK)   insol.

Caesium Salts.

Caesium metal,   v. sol.
"   alum,   insol.

Cerium Salts.

Cerium chloride, (G)   insol.
"   fluoride, (G)   insol.
"   nitrate, (G)(FK)   sl. sol.
"   oxide, (G)   insol.

Chromium Compounds.

Chromic acid, (G)(FK)   sl. sol.
Chromium chloride, (G)   sl. sol.
"   fluoride, (G)   insol.

Cobalt Salts.

Cobalt nitrate,   m. sol.
                              forms a yellow solution.
"   oxide,   insol.
                              soluble in ammonium nitrate.
"   carbonate, (G)   insol.
"   chloride, (G)(FK)   insol.
"   fluoride, (G)   insol.
"   sulphate, (G)(FK)   insol.

Copper Salts.

Copper metal, (G)(FK)   sl. action
Cupric acetate,   sl. sol.
"   arsenate,   insol.
"   arsenite,   insol.
"   ammonium chloride,   sl. sol.
"   formate,   sl. sol.
"   nitrate,   v. e. sol.
"   sulphate, cryst.,   insol.
"   oxide, (G)(FK)   sl. action
"   carbonate, (G)(FK)   insol.
"   chloride, (G)   insol.
"   chromate, (G)   insol.
"   ferrocyanide, (G)   insol.
"   fluoride, (G)   insol.
"   phosphate, (G)   insol.
"   sulphate, white, (G)   insol.
"   sulphide, (G)(FK)   insol.
Cuprous chloride,   sl. sol.
"   iodide,   v. sol.
"   oxide, (G)   sl. action
"   cyanide,(G)(FK)   m. sol.

Didymium Salts.

Didymium nitrate,   m. sol.

Glucinum Salts.

Glucinum carbonate, (G)	insol.
" chloride, (G)	insol.
" oxide, (G)	insol.
" sulphate, (G)	insol.

Gold Salts.

Gold chloride, (G)	sl. sol.

Iron Salts.

Iron, metallic, (G),	insol.
Ferric bromide,	sl. sol.
" iodide,	v. sol.
" pyrophosphate,	insol.
" sulphate,	insol.
Ferrous lactate,	sl. sol.
" sulphate,	insol.
" sulphide,	insol.
" valerianate,	sl. sol.

Lead Salts.

Lead acetate,	v. sol.
" bromide,	m. sol.
" carbonate,	insol.
" chloride,	sl. sol.
" formate,	m. sol.
" iodide,	v. e. sol.
" nitrate,	v. e. sol.
" oxide (litharge),	insol.
" peroxide,	insol.
" sulphide (galena),	insol.
" tartrate,	insol.
" chromate, (G)(FK)	insol.
" metal, (G)	insol.
" oxide, red, (G)(FK)	insol.
" fluoride, (G)	insol.
" iodate, (G)	insol.
" chromate, (G)(FK)	sl. sol.

Lithium Salts.

Lithium benzoate,	v. sol.
" bromide,	m. sol.
" carbonate,	insol.
" chloride,	sl. sol.
" iodide,	v. sol.
" nitrate,	v. e. sol.
" salicylate,	v. sol.
" metal, (G)(FK)	sol.

Magnesium Salts.

Magnesium bromide,	sl. sol.
" iodide,	v. sol.
" carbonate,	insol.
" nitrate,	v. e. sol.
" oxide,	insol.
" phosphate,	insol.
" sulphate,	insol.
" sulphite,	insol.
" metal, (G)	insol.
" basic chloride,(G)	sl. sol.

Manganese Salts.

Manganese carbonate,	insol.
" iodide,	m. sol.
" nitrate,	v. sol.
" metal, (G)	insol.
" chloride, (G)(FK)	insol.
" fluoride, (G)	insol.
" sulphate, (G)(FK)	insol.
" bromide,	insol.

Molybdenum Salts.

Molybdenum metal, (G)(FK)	insol.
" sulphide, (G)	insol.
Molybdic acid, (G)(FK)	insol.

Nickel Salts.

Nickel nitrate,	m. sol.
forms a purplish solution.	
" sulphate,	insol.
" metal, (G)	insol.
" chloride, (G)(FK)	insol.
" fluoride, (G)	insol.
" hydroxide, (G)	insol.
" oxide, (G)	insol.

Osmium Salts.

Osmium metal, (G)	insol.
Osmic acid, (G)	action.

Palladium Salts.

Palladium metal, (G)	insol.
" chloride, (G)	sl. sol.
" sulphide, (G)	insol.

Platinum Salts.

Platinum metal, (G)	insol.
Platinous chloride, (G)	sl. sol.
Platinic chloride, (G)	sl. sol.
" iodide, (G)	v. sol.
Platinum oxide, (G)	insol.

Phosphorus Compounds.

Phosphorus pentoxide,	insol.
Phosphorus, white, (G)(FK)	sol.
" red, (G)(FK)	insol.
Phosphoric acid, glac., (G)	insol.
Phosphorus trichloride, (G)(FK)	action.
" pentachloride, (G)(FK)	action.

Potassium Salts.

Potassium acetate,	sl. sol.
" carbonate,	insol.
" chlorate,	m. sol.
" cyanate,	v. e. sol.
" ethyl sulphate,	v. sol.
" ferricyanide,	insol.
" hydroxide,	insol.
" hypophosphite,	sl. sol.

Potassium iodate,	insol.
" metaphosphate,	insol.
" phenylsulphonate,	m. sol.
" metanitrobenzene-sulphonate,	m. sol.
" sulphate,	insol.
" sulphide,	m. sol.
" pyroantimonate,	insol.
" nitrite,	v. sol.
" nitroprusside,	v. sol.
" sulphite,	insol.
" metal, (G)(FK)	sol.
" bichromate,(G)(FK)	sl. sol.
" bromide, (G)(FK)	m. sol.
" chloride, (G)(FK)	sl. sol.
" chloriridate, (G)	insol.
" chromate, (G)(FK)	insol.
" cyanide, (G)(FK)	m. sol.
" ferrocyanide, (G)(FK)	insol.
" fluozirconate, (G)	insol.
" fluoride, (G)	v. sl. sol.
" iodide, (G)(FK)	v. e. sol.
" nitrate, (G)(FK)	v. sol.
" permanganate (G)(FK)	v. sol.
" silicofluoride, (G)	insol.
" sulphocyanate, (G)(FK)	v. sol.

Mercuric Salts.

Mercuric nitrate,	v. sol.
" fulminate,	v. e. sol.
" sulphocyanate,	v. e. sol.
" chloride, (G)(FK)	m. sol.
" cyanide, (G)(FK)	v. e. sol.
" iodide, (G)(FK)	v. e. sol.
" oxide, yellow, (G)(FK)	insol. sol. in ammonium nitrate.
" oxide, red, (G)	insol.
" bromide, (G)	m. sol.
" sulphate, (G)(FK)	insol.
" sulphide, (G)	insol.

Mercurous Salts.

Mercurous acetate, (G)	insol.
" iodide, (G)	v. sol.
" oxide,	v. e. sol.
" chloride, (G)(FK)	insol.
" nitrate, (G)(FK)	v. sol.
Mercury metal, (G)	v. sol.
	insol.

black precipitates are formed by the action of ammonia on mercurous salts.

Rubidium Salts.

Rubidium chloride,	v. sl. sol.
" metal, (G)(FK)	sol.
" fluoride, (G)	insol.

Silver Salts.

Silver acetate,	sl. sol.
" nitrite,	v. sol.
" thioethylcarbamate,	insol.
" metal, (G)	insol.
" carbonate, (G) (FK)	insol.
" chloride, (G)(FK)	sl. sol.
" chromate, (G)	insol.
" cyanide, (G)(FK)	m. sol.
" fluoride, (G)	sl. sol.
" iodide, (G)(FK)	v. sol.
" iodate, (G)	insol.
" oxide, (G)(FK)	insol.
" peroxide, (G)	insol.
" nitrate, (G)(FK)	v. sol.
" phosphate,	insol.
" sulphate, (G)(FK)	insol.
" vanadate, (G)	insol.
" arseuate, (G)	insol.
" bromide, (G)(FK)	m. sol.

Sodium Salts.

Sodium acetate,	sl. sol.
" bisulphate,	insol.
" bromide,	v. sol.
" carbonate,	insol.
" citrate,	insol.
" chlorate,	v. sol.
" ethyl sulphate,	v. sol.
" formate,	v. sl. sol.
" hydroxide,	insol.
" hypophosphite,	sl. sol.
" iodide,	v. e. sol.
" nitrate,	v. sol.
" nitrite,	v. sol.
" phenylsulphonate,	m. sol.
" propionate.	v. sl. sol.
" pyrophosphate,	insol.
" sulphate,	insol.
" sulphite,	insol.
" tungstate,	sl. sol.
" o-xylenesulphonate,	m. sol.
" valerianate,	insol.
" biborate,	insol.
" bromate,	m. sol.
" bichromate,	sl. sol.
" permanganate,	m. sol.
" phosphomolybdate,	insol.
" salicylate,	v. sol.
" thiosulphate,	m. sol.
" metal, (G)(FK)	sol.
" chloride, (G)(FK)	m. sol.

Strontium Salts.

Strontium chloride,	insol.
" nitrate,	v. sol.
" carbonate,	insol.
" sulphate,	insol.
" metal, (G)	insol.

Sulphur Compounds.

Sulphur, (G)(FK)	sol.
" chloride, (G)(FK)	m. sol.
Sulphur iodide,	v. sol.

Thallium Salts.

Thallium chloride,	insol.
" nitrate,	m. sol.
" metal, (G)(FK)	insol.
" fluoride, (G)	insol.
" peroxide, (G)	insol.

Tin Salts.

Stannic chloride, (G)	v. sol.
" oxide, (G)	insol.
Stannous chloride, (G)	part. sol.
" oxide, (G)	insol.
Tin metal, (G)	insol.

Titanium Salts.

Titanic acid, (G)	insol.
Titanium nitrocyanide, (G)	insol.
" oxide, black, (G)	insol.

Uranium Salts.

Uranium fluoride, (G)	sl. sol.
" nitrate, (G)	sl. action
" oxide, (G)	sl. action

Zinc Salts.

Zinc acetate,	m. sol.
" carbonate,	insol.
" chromate,	insol.
" ferrocyanide,	v. sl. sol.
" lactate,	v. sol.
" nitrate,	v. e. sol.
" oxide,	insol.
" phosphate,	insol.
" sulphate,	insol.
' sulphide, (blende)	insol.
" tartrate,	insol.
" bromide, (G)(FK)	v. sl. sol.
" chloride, (G)(FK)	insol.
" cyanide, (G)(FK)	v. sol.
" fluoride, (G)	insol.
" iodide, (G)(FK)	m. sol.

Miscellaneous.

Carbon, charcoal, (G)	insol.
" graphite, (G)	insol.
" bisulphide, (G) (FK)	action
" tetrabromide, (G)	v. sol.
" tetrachloride, (G)(FK)	miscible
" hexachloride, (G)	insol.
Iodine, (G)(FK)	sol.
Iodic acid, (G)(FK)	insol.
Indium metal, (G)	insol.
" black oxide, (G)	insol.

Lanthanum sulphate, (G)	insol.
Niobic acid, (G)	insol.
Osmiridium, (G)	insol.
Selenium, (FK)	sol.
Selenic acid,	insol.
Selenious acid, (G)	insol.
Silicon, cryst., (G)	insol.
" pptd., (G)	insol.
Tungsten, (G)	insol.
Tungstic acid, (G)	insol.
Thorium sulphate, (G)	insol.
Tellurium, (G)(FK)	insol.
Vanadic acid, (G)	insol.
Vanadium nitride, (G)	insol.
Water, (G)(FK)	miscible
Phosgene,	action

Paraffin Hydrocarbons.

Hexane,	insol.
Diisoamyl,	insol.
Paraffin, (G)	insol.

Halogen Derivatives.

Methyl iodide,	miscible
Chloroform, (G)(FK)	miscible
	reaction
Bromoform,	miscible
Iodoform,	v. e. sol.
Ethyl bromide,	m. sol.
" iodide,	m. sol.
Ethylidene chloride,	miscible
Ethylene bromide,	m. sol.
Tribromethane,	v. sol.
Isobutyl bromide,	m. sol.
Amyl bromide,	sl. sol.
Nitrotrichlormethane,	miscible

Alcohols.

Methyl alcohol,		miscible
Ethyl " (G)(FK)		miscible
Propyl "		miscible
Butyl "	normal,	miscible
" "	iso,	miscible
" "	tertiary,	miscible
Pentyl " (G)(FK)		miscible
Heptyl "		miscible
Octyl "		miscible
Cetyl "		insol.

Ethers.

Diethyl ether, (G)(FK)	miscible
Methylal,	miscible
Diamyl ether,	sl. sol.

Polyhydroxy Alcohols.

Ethylene glycol,	miscible
Propylene glycol,	miscible

Glycerine, (G)(FK)	miscible
Erythrite,	v. sl. sol.
Dulcite,	sl. sol.
Mannite,	sl. sol.

Aldehydes.

Acetaldehyde, (G)(FK)	miscible
Paraldehyde,	miscible
Aldehyde ammonia,	m. sol.
Chloral hydrate,	m. sol.
Bromal hydrate,	v. sol.
Chloral cyanhydrate,	v. sol.
Isobutyl aldehyde,	v. e. sol.
Valeric aldehyde,	v. sol.
Heptyl aldehyde,	m. sol.
Glyoxal,	insol.
Pinacone,	v. sol.
Oxymethylene,	insol.

Acids.

Formic acid,	miscible
Acetic acid,	m. sol.
Chloracetic acid,	v. sol.
Dichloracetic acid,	v. sol.
Trichloracetic acid,	v. e. sol.
Bromacetic acid,	v. sol.
Dibromacetic acid,	v. sol.
Propionic acid,	m. sol.
α-Brompropionic acid,	v. sol.
β-Brompropionic acid,	m. sol.
Butyric acid, normal,	m. sol.
Butyric acid, iso,	v. e. sol.
Valeric acid,	m. sol.
Caproic acid,	m. sol.
Oenanthylic acid,	sl. sol.
Caprylic acid,	sl. sol.
Capric acid,	v. sl. sol.
Pelargonic acid,	insol.
Myristic acid,	insol.
Palmitic acid,	insol.
Margaric acid,	insol.
Stearic acid,	insol.

Dibasic Acids.

Oxalic acid,	insol.
Malonic acid,	insol.
Succinic acid, (G)(FK)	insol.
Pyrotartaric acid,	insol.
Diacetsuccinic acid,	v. sol.
Dibromsuccinic acid,	sl. sol.

Ethereal Salts.

Ethyl formate,	miscible
Amyl "	miscible
Ethyl acetate,	miscible
Propyl "	miscible
Isobutyl "	miscible
Amyl "	v. e. sol.
Capryl "	sl. sol.

Methyl propionate,	miscible
Propyl "	v. e. sol.
Amyl "	m. sol.
Methyl butyrate,	miscible
Ethyl "	miscible
Amyl "	sl. sol.
Isobutyl "	m. sol.
Ethyl valerianate,	v. e. sol.
Isobutyl "	m. sol.
Amyl "	sl. sol.
Ethyl caprylate,	sl. sol.
" pelargonate,	sl. sol.
" orthoformate,	miscible
" oxalate,	v. e. sol.
rapidly forms oxamide.	
" malonate,	miscible
" succinate,	miscible
" lactate,	miscible
" tartrate,	miscible
" citrate,	miscible
" carbonate,	miscible
Tributyrin,	miscible
Amyl nitrite,	m. sol.

Cyanides.

Methyl cyanide,	miscible
Ethyl "	miscible
Cyanuric acid,	sl. sol.
Ethyl sulphocyanate,	miscible
Ethyl isosulphocyanate,	v. e. sol.
Paracyanogen, (G)	insol.

Amines.

Methylamine,	miscible
Trimethylamine,	miscible
Diethylamine,	m. sol.
Dipropylamine,	m. sol.
Amylamine,	miscible
Diamylamine,	sl. sol.
Tetramethylammonium iodide,	sl. sol.
Hydroxylaminehydrochloride,	v. sol.

Amido Acids.

Glycocoll,	v. sol.
Amidopropionic acid,	v. sol.
Leucine,	v. sol.
Sarcosine,	v. sol.
Tyrosine,	v. sol.

Acid Amides and Ureides.

Formamide,	v. e. sol.
Acetamide,	v. e. sol.
Propionamide,	v. e. sol.
Oxamide,	sl. sol.
Succinimide,	v. sol.
Asparagine,	m. sol.
Creatine,	m. sol.
Urea,	m. sol.

Urea nitrate,	v. sol.
Allylthiourea,	v. sol.
Sulphocarbanilide,	v. sol.
Uric acid, (G)(insol.)(FK)	m. sol.
Guanidine nitrate,	v. e. sol.
Theobromine,	m. sol.
Alloxantine,	m. sol.
Parabanic acid,	m. sol.
Dialuric acid,	m. sol.
Uramil,	v. sol.
Murexide,	m. sol.
Alloxan, (G)	v. sol.

Hydroxy Acids.

Glycollic acid,	v. sol.
Lactic acid,	v. sol.
Malic acid,	sl. sol.
Tartaric acid,	sl. sol.
Citric acid,	sl. sol.
Mucic acid,	m. sol.
Oxyisobutyric acid,	v. sol.

Sugars.

Arabinose,	m. sol.
Glucose,	v. sol.
Fructose,	v. sol.
Galactose,	m. sol.
Phenylglucosazone,	v. sol.
Sucrose, (G)(FK)	v. sol.
Lactose,	v. sol.
Maltose,	v. sol.
Raffinose,	v. sol.

Ethylene Derivatives.

Amylene, (G)	insol.
Allyl alcohol,	miscible
Allyl isosulphocyanide,	miscible
Oleïc acid,	insol.
Maleïc acid,	insol.
Fumaric acid,	insol.
Itaconic acid,	insol.
Citraconic acid,	sl. sol.
Mesaconic acid,	sl. sol.
Aconitic acid,	m. sol.
Crotonic acid,	m. sol.

Aromatic Hydrocarbons.

Benzene,	m. sol.
Toluene,	sl. sol.
o-Xylene,	v. sl. sol.
m- "	v. sl. sol.
p- "	v. sl. sol.
Ethylbenzene,	v. sl. sol.
Mesitylene, (G)(FK)	insol.
Cumene,	insol.
Pseudocumene,	insol.
Cymene,	insol.
Diphenyl,	v. sl. sol.
Diphenylmethane,	insol.
Triphenylmethane,	insol.

Halogen Derivatives.

Chlorbenzene,	v. sl. sol.
Brombenzene,	v. sl. sol.
Iodbenzene,	v. sl. sol.
Hexachlorbenzene,	v. sl. sol.
Dibrombenzene,	v. sl. sol.
p-Chlortoluene,	v. sl. sol.

Nitro Derivatives.

Nitrobenzene,	v. sol.
Dinitrobenzene,	m. sol.
o-Nitrotoluene,	m. sol.
p- "	v. sl. sol.
1-2-4-Dinitrotoluene,	sl. sol.
Trinitrotoluene, ·	m. sol.
m-Nitrochlorbenzene,	sl. sol.
p- "	sl. sol.
m-Nitro-*p*-chlortoluene,	m. sol.

Amido Derivatives.

Aniline,	miscible
o-Toluidine,	miscible
p- "	v. sol.
Xylidine, asym. *m*,	sl. sol.
Dimethylaniline,	v. sl. sol.
Diethylaniline,	v. sl. sol.
Methyldiphenylamine,	sl. sol.
m-Nitraniline,	v. sol.
p- "	v. sol.

Phenols.

Phenol,	v. sol.
o-Cresol,	miscible
m- "	miscible
p- "	miscible
Pyrocatechin,	v. e. sol.
Resorcin,	v. e. sol.
Hydroquinone,	v. sol.
Pyrogallol,	v. e. sol.
Orcin,	v. sol.
Guaiacol,	miscible
Anisol,	miscible
Phenetol,	miscible
Thymol,	v. sol.
Menthol,	m. sol.

Substituted Phenols.

o-Nitrophenol,	v. e. sol.
p- "	v. sol.
1-2-4-Dinitrophenol,	v. sol.
Trinitrophenol,	v. sol.
p-Nitroanisol,	sl. sol.
Eugenol,	m. sol.
Anethol,	sl. sol.
o-Amidophenol,	v. sol.
p- "	v. sol.

Alcohols.

Benzyl alcohol,	miscible

Cinnamic alcohol,	miscible

Ethers.

Benzylethyl ether,	sl. sol.

Aldehydes.

Benzaldehyde,	v. sol.
Anisaldehyde,	miscible
m-Nitrobenzaldehyde,	v. e. sol.
Cinnamic aldehyde,	miscible
Vaniline,	v. sol.
Heliotropine,	v. sol.

Monobasic Acid.

Benzoic acid,	v. sol.
Benzoic anhydride,	v. sol.
a-Toluic acid,	v. sol.
o- " "	v. sol.
m- " "	v. sol.
p- " "	m. sol.
Cinnamic acid,	m. sol.

Substitution-Products.

m-Brombenzoic acid,	v. e. sol.
o-Nitrobenzoic acid,	m. sol.
m- " "	m. sol.
p- " "	sl. sol.
o-Amidobenzoic acid,	v. sol.
m- " "	v. sol.
p- " "	v. sol.
o-Hydroxybenzoic acid,	v. e. sol.
m- " "	v. sol.
p- " "	v. sl. sol.
o-Nitrocinnamic acid,	v. sol.
Nitrophenylpropiolic acid,	m. sol.
Gallic acid,	m. sol.
Anisic acid,	m. sol.
Coumarin,	m. sol.

Dibasic Acids.

o-Phthalic acid,	v. sl. sol.
p- " "	v. sl. sol.
Phthalimide,	v. e. sol.

Ethereal Salts.

Methyl benzoate,	miscible
Ethyl benzoate,	v. e. sol.
Isobutyl benzoate,	insol.
Amyl benzoate,	insol.
Methyl salicylate,	m. sol.
Phenyl cyanide,	miscible
Benzyl cyanide,	miscible
p-Cyantoluene,	v. sol.
Phenyl acetate,	miscible
Phenyl salicylate,	sl. sol.
Phenyl isosulphocyanate,	m. sol.
Ethylphenyl carbamate,	v. e. sol.

Sulphonic Acids.

Benzenesulphon chlorid,	action

o-Amidobenzenesulphonic acid,	
	v. e. sol.
m-Amidobenzenesulphonic acid,	
	v. e. sol.
p-Amidobenzenesulphonic acid,	
	v. e. sol.
Benzoicsulphinide (saccharin),	m. sol.

Acid Amides and Anilides.

Formanilide,	v. sol.
Acetanilide,	v. sol.
Benzamide,	v. sol.
Benzanilide,	sl. sol.
Hippuric acid,	v. sol.
p-Acettoluide,	sl. sol.
Benzenesulphonamide,	v. e. sol.
Carbazol,	m. sol.

Naphthalene and Derivatives.

Naphthalene, (G)(FK)	v. sl. sol.
a-Naphthol,	m. sol.
β- "	sl. sol.
a-Naphthylamine,	v. sol.
β- "	m. sol.
Nitroso-β-naphthol,	m. sol.
Acetnaphthalide,	sl. sol.

Pyridine and Quinoline.

Pyridine,	miscible
Picoline,	miscible
Collidine,	miscible
Nicotine,	m. sol.
Dihydrocollidinedicarbonic- acid diethylester,	sl. sol.
Quinoline,	miscible
Isoquinoline,	sl. sol.

Terpenes.

Terebene,	insol.
Carvol,	sl. sol.
Carvene,	sl. sol.
Pinene,	insol.
Sylvestrene,	insol.
Terebenthene,	insol.
Borneol camphor,	m. sol.
Camphoric acid,	insol.

Unclassified.

Iodosobenzene,	sl. sol.
Iodoxybenzene,	m. sol.
Diphenyliodonium iodide,	sl. sol.
Diphenyliodonium chromate,	insol.
Acetophenone,	m. sol.
Quinone,	m. sol.
Chloranil,	m. sol.
Benzil,	m. sol.
Benzoin,	insol.
β-Benzyldioxime,	v. e. sol.
Haematoxylin,	m. sol.
Haemaglobin,	sl. sol.

Cholesterine.	insol.	Cinchona,	insol.
Amygdaline,	v. sol.	Codeia,	m. sol.
Codea nitrate,	insol.	Cubebine,	m. sol.
Cocaine,	insol.	Meconine,	insol,
Cocaine hydrochloride,	m. sol.	Morphia,	insol.
Cubebina,	v. sol.	Narcotine,	insol.
Digitaline,	v. e. sol.	Quinine,	insol.
Phloridzine,	v. e. sol.	" hypophosphite,	m. sol.
Picrotoxine,	v. e. sol.	Quinine iodide,	insol.
Piperidine,	sl. sol.	Quinine sulphate, (G)(FK)	insol.
Piperine,	insol.	Quinidia,	insol.
Salicine,	v. sol.	Theine,	sl. sol.
Santonine,	insol.	Tannic acid,	sl. sol.
Strychnine,	insol.	Indigo, (G)	sl. sol.
" acetate,	insol.	Gutta percha, (G)	action
" bromide,	insol.	Starch, (G) " swells up and mixes as in	
" chloride,	insol.	water."	
Anthracene,(G)(FK)	insol.	Isinglass, (G)	" semifluid."
Phenanthrene,	insol.	Camphor, (G)	v. sol.
Anthraquinone,	insol.	Gum copal (G)	v. sl. sol.
Alizarine,	m. sol.	Gun cotton,(G)	sl. sol.
Brucia,	m. sol.	Bengal silk, (G)	insol.
Cinchonidia,	sl. sol.		

Experiments at Higher Temperatures.

The statements of Gore[1] to the effect that sulphur and phosphorus are soluble in ammonia have led us to study the action of ammonia on these and some other substances at temperatures considerably above the boiling-point of the solvent at atmospheric pressure. In making the tests a glass tube sufficiently strong to withstand the pressure was placed in a bath of liquid ammonia and then charged with a small quantity of the substance to be tested, together with 2 or 3 cc. of liquid ammonia. The tube was sealed before the blowpipe, after which it was removed from the refrigerating-bath and allowed to warm up to the temperature of the laboratory. It was found that a number of substances, which at —38° were not perceptibly soluble, dissolved abundantly at 25°.

Results.

Sulphur.—Sulphur dissolves slowly, forming a dirty green colored solution, which on refrigeration changes to a red color, without, however, the separation of any solid from the solution. The solution is a conductor of electricity. On evaporation a red liquid is left behind which mixes with water with the separation of sulphur.

[1] *Loc. cit.*

Selenium.—Selenium dissolves very slowly, forming a solution which resembles the sulphur solution.

Phosphorus.—Phosphorus is acted upon by ammonia at 25°, but much more slowly than is sulphur. It forms a dark brown, almost opaque, solution which deposits no solid on being subjected to refrigeration. The solution is a conductor of electricity.

Hexane.—Hexane is very slightly soluble in ammonia at 25°. On cooling the solution becomes milky.

Benzene.—Benzene, which is but moderately soluble at —38°, is extremely soluble at 25°. On cooling the solution a solid, presumably benzene, crystallizes out.

Metaxylene.—Xylene is but very slightly soluble at —38°. At the higher temperature it is miscible in all proportions. On cooling the solution, the xylene separates abundantly.

Triphenylmethane.—This compound, which is not perceptibly soluble at —38°, is readily soluble at the higher temperature. The hydrocarbon crystallizes out when the solution is cooled.

Naphthalene.—Evaporation of a portion of solvent which, at atmospheric pressure, had been in contact with powdered naphthalene, showed the substance to be very slightly soluble. It dissolves abundantly when the solvent is warmed, separating again when the solution is cooled.

Anthracene.—Anthracene is but very slightly soluble at 25°.

Pinene.—Pinene dissolves slightly at 25°. When cooled, the solution becomes milky in consequence of separation of the solute.

Chlorbenzene and Iodobenzene.—These two halogen products, which are but very slightly soluble in ammonia at —38°, are miscible in all proportions at the higher temperature.

Dibrombenzene.—Dibrombenzene dissolves very easily at 25°. When the solution is cooled the substance separates out rapidly in beautifully formed crystals.

Phthalic Acid.—The phthalic acid crystals are disintegrated, forming, probably, ammonium phthalate, which is insoluble in ammonia even at a temperature of 25°.

Benzanilide.—Benzanilide is more soluble at 25° than it is at —38°.

Stearic Acid.—Stearic acid is very slightly soluble at 25°. On cooling the solution a slight separation of solid takes place.

Succinic Acid.—The crystals of the acid are disintegrated by the ammonia forming presumably ammonium succinate, which, however, remains undissolved at 25°.

Parahydroxybenzoic Acid.—This acid, which is but slightly soluble at —38°, dissolves abundantly at 25°. It separates slowly when the solution is cooled.

Cadmium Iodide.—Cadmium iodide is not perceptibly more soluble at the higher temperature than at —38°.

Ammonium Chromate.—This salt is somewhat more soluble at the higher temperature. On cooling the solution, yellow crystals separate on the walls of the tube.

Potassium Chromate.—Potassium chromate is insoluble at the higher as well as the lower temperature.

University of Kansas,
Lawrence, June, 1898.

DETERMINATION OF THE MOLECULAR RISE IN THE BOILING-POINT OF LIQUID AMMONIA.

By E. C. Franklin and C. A. Kraus.

In view of the position occupied by liquid ammonia as a solvent, determinations of the molecular elevation of its boiling-point produced by substances in solution, become a matter of interest. For the purpose of measuring the constant experimentally, a modified form of Beckmann's boiling-point apparatus, was devised and used with fairly satisfactory results. The difficulties inherent in the boiling-point method certainly persist when the solvent used boils 60° below the laboratory temperature, and, in further consideration of the surprisingly small effect of a dissolved solute on the boiling-point of the solvent, we consider the measurements made to be fairly satisfactory.

Apparatus.

Fortunately for our purpose, the boiling-point of ammonia at atmospheric pressure lies above the freezing-point of mercury.

It was consequently found to be a comparatively simple matter to adapt the Beckmann method to the determination of the boiling-point elevation of ammonia solutions. After several attempts with various modifications of the apparatus, the form described in the following was finally devised and used in making the determinations given in this paper:

For the boiling-vessel a vacuum-jacketed Dewar tube was used. This is represented one-half the natural size by Fig. 1. The vessel has a capacity of 25 to 30 cc. when filled to a point half way between the top of the platinum cylinder and the cork stopper. AA are heavy platinum wires sealed in with red lead glass. B is a coil of small platinum wire connecting the interior ends of the two heavy wires, the joints being secured by means of gold solder. C is the filling-material consisting, in these experiments, of a layer of garnets sufficient to protect the coil B, covered with a layer of the platinum tetrahedra of Beckmann.[1] D is a platinum cylinder covering the bulb of the thermometer, and introduced for the purpose of protecting the thermometer from the effects of radiation.[2] E is an ordinary Beckmann thermometer made by F. O.
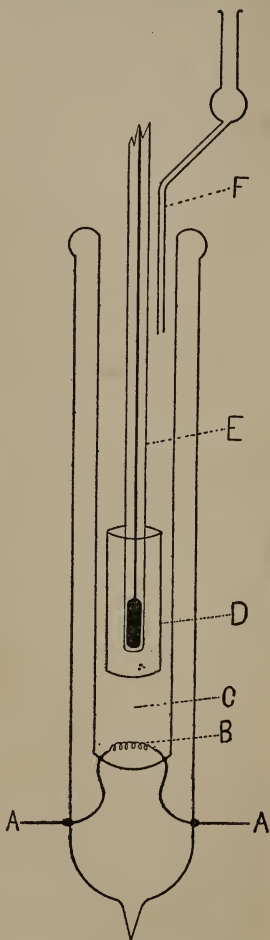
Fig. 1.

[1] Ztschr. physikal. Chem., **21**, 284.
[2] Jones: This JOURNAL, **19**, 582.

R. Götze, in Leipsic, for determinations by the boiling-point method. It is held in place by a perforated cork stopper provided with a small tube, F, for the escape of the ammonia vapor. In some experiments a drying-tube containing soda-lime was attached to F. It was not considered feasible to condense the ammonia vapor and to return it to the boiling-tube as is done with ordinary solvents. It was consequently decided to allow the vapors to escape, and to determine the amount of solvent present after each boiling-point measurement, by weighing the whole piece of apparatus with its contents. For this purpose a balance was placed on a stable frame above the working table, a hole was cut through the bottom of the balance-case, and the boiling-tube with the thermometer in place was suspended by means of a wire from the arm of the balance. A battery, rheostat, and ammeter are conveniently placed for the purposes respectively of furnishing, regulating, and measuring the current used in boiling the liquid in the boiling-tube.

The considerably greater quantity of mercury contained in the bulb of the thermometer when used in measuring temperatures as low as the boiling-point of ammonia would have the effect of giving scale readings on a thermometer made to be used at much higher temperatures, greater than the true differences in temperature. Measurements made by Grütz-macher[1] give as a result, that between the temperatures of $-35°$ and $-30°$ with the mercury column at the same temperature, the value of one scale division on the thermometer is equal to $0.982°$; with the mercury column at $0°$ and the bulb at $-35°$ to $-30°$, one scale division was found to be equal to $0.977°$. In our experiments the temperature of a portion of the mercury column was about $17°$ to $22°$, which would further slightly diminish the value of a scale division to about $0.975°$. However, this correction has not been introduced into the tables accompanying this paper.

Although the liquid boils gently as the effect of heat conducted and radiated to the interior of the tube, the ammonia remains considerably superheated, as a few attempts to get

[1] Grützmacher: Ztschr. für Instrumentenkunde, 1896, 202; and E. Beckmann: Ztschr. physikal. Chem., 21, 253.

concordant measurements of boiling-point elevations soon convinced us. More vigorous boiling was brought about by passing a current of electricity through the wire ABA. The temperature falls with increasing current more and more slowly, until an expenditure of about 20 watts was reached. Currents above this strength produced no further depression of the thermometer.

When the attempt was made to determine accurately the boiling-point of the solvent, it was found that the mercury fell continuously in the capillary of the thermometer as the solvent boiled away. The depression of the mercury was slow, but was distinctly measurable. In order to make corrections for this effect, a scale was affixed to the tube on which was marked the contents in grams, from the lowest point at which measurements were made to the highest ; from 10 to 20 grams. It was found as the mean of several experiments that the difference between the apparent boiling-points when the tube was charged with 10 and 20 grams of solvent respectively, was 0.042°, giving a correction of 0.004° to be added to successive measurements differing from each other by one scale division.

The cause of this behavior is undoubtedly to be found in the diminishing weight of the supernatant liquid as the solvent boils away. Further than this, there is the factor of the varying specific gravity of the solution which must affect the correction to be made, and this effect, in the case of concentrated solutions, may not be inconsiderable. No attempts at corrections for variations from this latter cause have, however, been made.

Making the Determinations.

The boiling-tube, tared with the thermometer, garnets, and platinum cylinder, was charged with solvent from the stock cylinder as follows : In Fig. 2, L is the stock cylinder, M is the discharging valve, N is the boiling-tube, and O is a bottle containing water. On opening the valve M, a portion of the ammonia in the form of gas passes through N into O, and is there absorbed and saved, while the liquid collects in the tube N. After collecting from 16 to 18 grams of solvent in

the boiling-tube it is removed to its position under the bal-
ance-case, the thermometer is introduced, and the whole left
at rest until the thermometer has cooled down to the temper-
ature of the slowly boiling liquid.   The current which is then
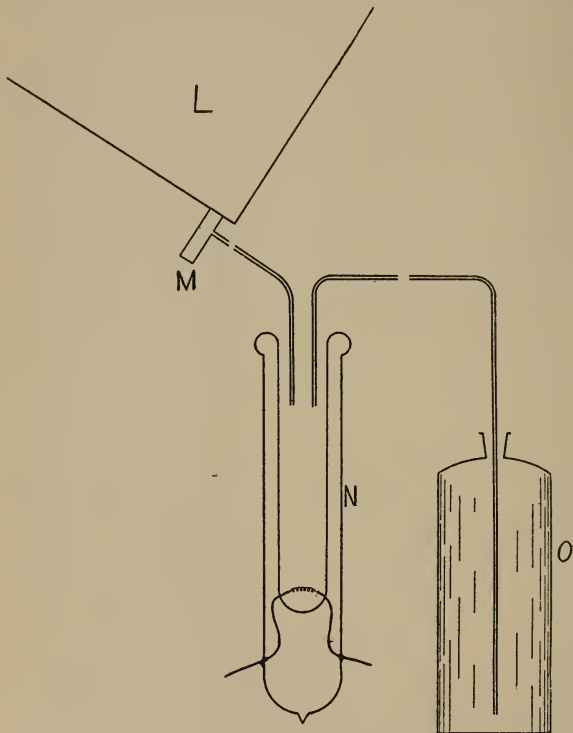
Fig. 2.

turned on, causes a vigorous boiling of the solvent and a rapid
decline of the temperature.   As soon as the mercury has be-
come stationary and is not further affected by gentle rapping
of the brass cap of the thermometer, the temperature is read,
and immediately thereafter the current is stopped, and the

scale on the boiling-tube noted.   The cork bearing the thermometer is then removed sufficiently to permit the introduction of the solute, which is accomplished in the case of liquids by means of Beckmann's pipette, in the case of those solids which permit it, in the form of compressed tablets, while other solids are introduced by weighing crystal fragments from specimen tubes.   These weights are given in the tables below under '' Gm. Solute.''   The thermometer is then replaced in position, and the operation of determining the boiling-point is again carried out as described above, the proper correction being made for the solvent boiled away. As soon as this is accomplished, the boiling-tube is loosened from its fastenings and weighed.   The weight of the solute, plus the weight of the empty apparatus, subtracted from the weight thus obtained, gives the weight of the solvent.   These values are given in the tables under '' Gm. Solvent.''   The experiment as above described is repeated until a sufficient number of determinations have been made.   The values under '' Constant'' are calculated by means of the formula,

$$\frac{\text{Gm. solvent} \times \text{elevation} \times \text{mol. wt.}}{\text{Gm. solute} \times 100}$$

The remaining columns need no explanation.

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
		1. Water.			
16.05	0.1469	0.92	5.00	0.174	3.42
15.17	0.1992	1.31	7.28	0.256	3.51
14.32	0.2626	1.83	10.17	0.356	3.50
13.58	0.3745	2.76	15.33	0.529	3.45
12.85	0.4106	3.20	17.78	0.613	3.45
11.91	0.5528	4.64	25.78	0.886	3.44
11.22	0.5911	5.27	29.27	1.009	3.45
10.36	0.8431	8.14	45.22	1.554	3.44
9.87	0.8431	8.54	47.44	1.631	3.44
9.13	1.1014	12.06	67.03	2.308	3.45
8.27	1.6261	19.66	109.22	3.852	3.53

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
		2. Water.			
15.96	0.2399	1.51	8.39	0.254	3.04
14.65	0.4006	2.74	15.22	0.497	3.27
13.28	0.5346	4.03	22.39	0.736	3.29
11.93	0.7792	6.53	36.28	1.210	3.33
10.96	0.9342	8.52	47.32	1.604	3.39
10.00	1.0542	10.53	58.55	1.987	3.39
9.07	1.0542	11.63	64.55	2.199	3.42
19.79	1.0542	5.33	29.61	1.011	3.42
18.47	1.0542	5.71	31.72	1.078	3.40
16.97	1.0542	6.21	34.50	1.116	3.38
15.60	1.0542	6.76	37.55	1.272	3.39
14.07	1.0542	7.49	41.61	1.409	3.39
11.78	1.0542	8.95	49.72	1.663	3.29
10.84	1.3149	12.13	67.39	2.300	3.42
9.92	1.6473	16.60	92.22	3.447	3.74
8.71	1.6473	18.91	105.05	3.966	3.78
		3. Ethyl Alcohol.			
16.84	0.0642	0.38	0.83	0.019	2.24
15.98	0.2550	1.60	3.47	0.108	3.11
15.23	0.3534	2.31	5.02	0.161	3.20
14.54	0.4584	3.15	6.83	0.230	3.36
13.83	0.6155	4.45	9.67	0.321	3.32
13.04	0.8328	6.39	13.90	0.463	3.34
12.33	1.0876	8.82	19.17	0.645	3.36
11.80	1.2002	10.17	22.11	0.800	3.62
11.12	1.3772	12.38	26.91	0.905	3.36
10.51	1.5365	14.63	31.80	1.071	3.37
9.97	1.6212	16.26	35.22	1.189	3.37
9.50	1.7750	18.68	40.61	1.384	3.41
8.96	1.9660	21.94	47.70	1.611	3.38
8.48	2.2680	26.74	58.13	1.961	3.38
7.99	2.5372	31.75	69.02	2.317	3.36
7.52	2.9004	38.56	83.83	2.827	3.38
6.73	3.0170	44.83	97.46	3.202	3.29
		4. Propyl Alcohol.			
14.13	0.0702	0.49	0.81	0.028	3.38
13.26	0.2420	1.83	3.05	0.106	3.49
11.79	0.5585	4.74	7.90	0.261	3.31
10.65	0.7182	6.74	11.23	0.371	3.30

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
9.70	0.9514	9.81	16.35	0.527	3.22
8.35	0.9514	11.39	18.95	0.612	3.22
18.52	0.9514	5.14	8.57	0.294	3.43
15.95	0.9514	5.83	9.72	0.329	3.31
14.89	1.1875	7.98	13.30	0.436	3.28
13.77	1.4332	10.41	17.35	0.565	3.26
12.37	1.7305	14.00	23.33	0.744	3.19
11.37	2.0319	17.87	29.78	0.919	3.09
10.57	2.3310	22.05	35.92	1.107	3.01
9.79	2.6872	27.45	45.75	1.346	2.94
8.87	3.0765	34.69	57.82	1.649	2.85
8.07	3.0765	38.13	66.55	1.797	2.83
7.46	3.5355	47.40	79.00	2.222	2.81
6.96	3.5355	50.81	84.68	2.378	2.81
6.31	3.5355	56.04	93.40	2.572	2.75

5. Phenol.

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
15.94	0.1141	0.74	0.79	0.028	3.68
13.91	0.3326	2.39	2.54	0.086	3.38
12.53	0.7951	6.31	6.71	0.200	2.98
11.68	1.2791	11.37	12.10	0.373	3.08
10.08	1.5957	15.83	16.84	0.509	3.02
9.20	1.5957	17.35	18.46	0.547	2.97
16.15	1.5957	9.88	10.51	0.334	3.18
14.29	1.5957	11.17	11.88	0.363	3.05
13.31	1.9102	14.35	15.26	0.480	3.14
12.14	1.9102	15.73	16.73	0.512	3.06
11.30	2.4448	21.64	23.02	0.715	3.10
8.68	2.4448	28.17	29.97	0.820	2.73
7.86	2.4448	31.11	33.10	0.914	2.76

6. Pyrocatechin.

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
15.51	0.1142	0.74	0.67	0.012	1.79
13.76	0.2605	1.89	1.72	0.045	2.67
12.65	0.5652	4.47	4.06	0.132	3.25
11.77	0.7811	6.64	6.04	0.198	3.28
10.69	1.0299	9.64	8.76	0.280	3.20
8.97	1.0299	11.48	10.44	0.344	3.30
18.59	1.0299	5.54	5.04	0.168	3.34
14.09	1.0299	7.31	6.65	0.210	3.16
12.87	1.3759	10.69	9.72	0.314	3.23
12.17	1.3759	11.31	10.28	0.328	3.19

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
11.19	2.0084	17.94	16.31	0.524	3.21
10.41	2.4862	23.88	21.71	0.690	3.18
9.16	2.4862	27.14	24.67	0.768	3.11

7. *Resorcin.*

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
17.32	0.1757	1.02	0.93	0.032	3.47
16.34	0.4592	2.81	2.55	0.085	3.33
14.69	0.4592	3.13	2.85	0.103	3.62
13.62	0.8265	6.07	5.50	0.194	3.52
12.77	0.8265	6.47	5.88	0.212	3.60
11.25	1.1547	10.26	9.33	0.327	3.59
10.15	1.1547	11.38	10.35	0.370	3.58
9.43	1.4687	15.58	14.16	0.497	3.51
8.63	1.4687	17.02	15.47	0.541	3.50
7.23	1.4687	20.32	18.47	0.645	3.49

8. *Hydroquinone.*

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
17.95	0.1002	0.56	0.51	0.024	4.73
16.45	0.2682	1.63	1.48	0.056	3.78
14.97	0.5314	3.55	3.24	0.122	3.78
13.77	0.6517	4.73	4.30	0.162	3.77
12.81	0.8306	6.48	5.89	0.224	3.80
11.76	1.0401	8.84	8.04	0.307	3.82
10.67	1.2402	11.62	10.56	0.403	3.81
9.91	1.4113	14.24	12.96	0.497	3.82
9.09	1.4113	15.52	14.11	0.543	3.85
17.64	1.4113	8.00	7.27	0.304	4.18
16.29	1.4113	8.66	7.86	0.328	4.17
14.31	1.4113	9.86	8.96	0.366	4.08
13.46	1.8166	13.50	12.27	0.492	4.01
12.00	1.8166	14.45	13.14	0.558	4.27
10.70	1.8166	16.98	15.44	0.630	4.08
9.28	1.8166	19.58	17.80	0.720	4.04
8.08	1.8166	22.49	20.45	0.839	4.10

9. *Hydroquinone.*

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
13.44	0.1052	0.78	0.71	0.019	2.81
12.57	0.2369	1.88	1.71	0.061	3.57
11.33	0.6657	5.88	5.33	0.189	3.50
10.27	1.2243	11.92	10.83	0.398	3.67
8.78	1.2243	13.94	12.67	0.446	3.52
17.93	1.2243	6.83	6.21	0.220	3.54
15.95	1.2243	7.67	6.97	0.262	3.76

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
13.78	1.2243	8.88	8.07	0.311	3.85
11.84	1.2243	10.34	9.40	0.352	3.75
10.00	1.2243	12.20	11.10	0.420	3.77
8.52	1.7780	20.87	18.97	0.719	3.79

10. Sugar.

15.61	0.0693	0.46	0.13	0.007	5.39
14.82	0.2548	1.72	0.53	0.019	3.18
13.99	0.6481	4.63	1.36	0.047	3.25
13.03	1.0547	8.10	2.37	0.080	3.25
11.82	1.5069	12.75	3.73	0.126	3.30
11.06	1.6089	14.55	4.25	0.148	3.41
10.30	2.3095	22.43	6.56	0.237	3.57
9.64	2.6523	27.51	8.04	0.301	3.71
8.76	3.3905	38.71	11.32	0.448	3.93
7.74	4.6151	59.64	17.44	0.761	4.35
6.89	4.6151	66.99	19.60	0.885	4.52
6.09	4.6151	75.79	22.16	1.042	4.70

11. Sugar.

17.35	0.0480	0.28	0.08	0.000	0.00
15.83	0.7382	4.66	1.37	0.039	2.90
14.44	1.4308	9.91	2.90	0.113	3.90
13.31	2.1426	16.10	4.71	0.180	3.82
11.95	2.8771	24.07	7.04	0.271	3.85
11.13	3.2691	30.05	8.79	0.330	3.85
9.90	3.8325	38.72	11.32	0.467	4.12
8.97	3.8325	42.73	12.49	0.527	4.22
18.51	3.8325	20.71	6.06	0.228	3.77
16.52	3.8325	23.20	6.78	0.263	3.88
14.37	3.8325	26.67	7.80	0.303	3.89
12.67	3.8325	30.25	8.84	0.357	4.04
11.18	3.8325	34.28	10.02	0.425	4.24
9.58	3.8325	40.01	11.70	0.502	4.29
8.25	3.8325	46.46	13.58	0.600	4.42
7.47	3.8325	51.17	14.96	0.676	4.52

12. Urea.

16.54	0.0284	0.17	0.29	0.015	5.24
15.77	0.1339	0.85	1.42	0.054	3.82
15.11	0.2850	1.89	3.15	0.100	3.18
14.49	0.5154	3.56	5.93	0.189	3.19

Gm. solvent.	Gm. solute	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
13.78	0.7263	5.27	8.78	0.274	3.12
13.07	1.0375	7.95	13.25	0.408	3.08
12.36	1.2086	9.78	16.30	0.486	2.98
11.69	1.4906	12.75	21.25	0.615	2.89
11.16	1.5678	14.05	23.42	0.663	2.83
10.51	1.8193	17.31	28.85	0.782	2.71
9.96	2.1244	21.32	35.53	0.904	2.54
9.94	2.3724	26.53	44.22	0.997	2.26

13. Urea.

Gm. solvent.	Gm. solute	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
13.94	0.4120	2.98	4.97	0.167	3.37
13.35	0.4120	3.09	5.15	0.177	3.44
12.63	0.7438	5.89	9.82	0.313	3.19
11.99	1.0157	8.46	14.10	0.433	3.07
11.33	1.0157	8.97	14.95	0.452	3.02
10.38	1.0157	9.79	16.32	0.484	2.97
9.75	1.0157	10.42	17.37	0.520	2.99
8.43	1.0157	12.05	20.08	0.587	2.92
7.29	1.0157	13.93	23.22	0.669	2.88
6.78	1.0157	14.95	24.92	0.714	2.86
6.19	1.0157	16.41	27.35	0.760	2.78
5.43	1.0157	18.70	31.17	0.854	2.74

14. Pyridine.

Gm. solvent.	Gm. solute	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
17.64	0.2138	1.21	1.53	0.050	3.26
16.49	0.2138	1.30	1.64	0.049	2.39
15.20	0.5994	3.94	5.00	0.164	3.28
14.10	0.5994	4.25	5.38	0.171	3.18
12.97	1.0844	8.36	10.58	0.321	3.03
12.22	1.0844	8.75	11.07	0.342	3.04
11.30	1.6004	14.16	17.92	0.513	2.86
10.59	1.9576	18.48	23.39	0.646	2.82
9.81	2.4151	24.62	31.16	0.818	2.60
9.06	2.9046	32.06	40.58	1.004	2.47
8.29	3.3648	40.58	51.50	1.211	2.36
7.60	3.8971	51.28	64.66	1.423	2.19
6.92	4.4814	64.76	80.97	1.681	2.05
6.14	5.2166	85.08	107.70	2.031	1.88
5.29	5.2166	98.74	124.93	2.240	1.79

15. Aniline.

Gm. solvent.	Gm. solute	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
17.90	0.2928	1.64	1.55	0.069	3.92
16.94	0.5370	3.17	3.41	0.123	3.61
15.96	0.7428	4.65	5.00	0.169	3.38

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
14.66	0.7428	5.07	5.45	0.185	3.40
13.73	1.0727	7.82	8.41	0.286	3.40
12.80	1.3046	10.15	10.91	0.365	3.34
11.99	1.6146	13.47	14.49	0.475	3.28
11.04	2.0144	18.24	19.61	0.634	3.23
10.10	2.6763	26.50	28.50	0.904	3.18
9.16	2.9880	32.62	35.08	1.095	3.12

16. Ortho-nitrophenol.

13.65	0.1026	0.75	0.54	0.027	4.99
12.72	0.3624	3.09	2.22	0.076	3.43
11.93	0.7670	6.43	4.62	0.157	3.39
11.15	1.2079	10.83	7.78	0.263	3.38
10.08	2.1302	21.13	15.20	0.499	3.28

17. Acetic Acid.

15.60	0.0328	0.21	0.35	0.013	3.77
13.62	0.2717	1.99	3.32	0.073	2.18
11.90	0.6902	5.80	9.67	0.187	1.90
10.00	1.2504	12.50	20.83	0.334	1.55
19.15	1.2504	6.53	10.88	0.223	2.01
17.25	1.2504	7.25	12.08	0.239	1.94
13.29	1.2504	9.41	15.67	0.297	1.85
10.59	1.2504	11.80	19.67	0.346	1.70
9.15	1.2504	13.66	22.77	0.395	1.67
8.12	1.2504	15.40	25.67	0.424	1.58

18. Sodium Acetate.

16.26	0.0441	0.27	0.38	0.014	3.71
15.04	0.0799	0.53	0.74	0.025	3.40
13.65	0.1930	1.41	1.96	0.060	3.10
10.51	0.3447	3.28	4.56	0.092	2.15

19. Benzene.

17.09	0.2690	1.57	2.01	0.064	3.17
15.62	0.5675	3.63	4.66	0.133	2.86
14.35	0.7150	4.98	6.38	0.164	2.57
13.11	0.7941	6.04	7.74	0.195	2.51
11.82	0.7941	6.70	8.60	0.213	2.47
10.84	0.7941	7.30	9.36	0.237	2.52
9.36	0.7941	8.28	10.61	0.263	2.47
8.53	0.7941	9.28	11.90	0.297	2.49
7.66	0.7941	10.33	13.24	0.321	2.42

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
15.91	0.7941	4.97	6.37	0.179	2.80
13.31	0.7941	5.95	7.63	0.199	2.60
11.76	0.7941	6.73	8.63	0.223	2.58
10.37	0.7941	7.63	9.77	0.242	2.47
9.41	0.7941	8.41	10.78	0.266	2.46
8.32	0.7941	9.51	12.19	0.300	2.45
7.76	0.7941	10.20	13.07	0.317	2.42

20. Benzene.

17.01	0.2386	1.40	1.79	0.038	2.21
15.56	0.5390	3.55	4.55	0.113	2.54
14.49	0.7422	5.24	6.72	0.176	2.68
13.50	0.8850	6.56	8.41	0.225	2.68
11.97	0.8850	7.39	9.47	0.238	2.51
10.46	0.8850	8.46	10.84	0.262	2.41
9.03	0.8850	9.80	12.56	0.283	2.25
7.04	0.8850	12.57	16.11	0.319	1.96
17.76	0.8850	4.98	6.38	0.134	2.10
16.46	0.8850	5.38	6.89	0.156	2.26
14.91	0.8850	5.94	7.61	0.166	2.17
13.22	0.8850	6.69	8.59	0.189	2.20
10.81	0.8850	8.19	10.50	0.220	2.08
9.54	0.8850	9.28	11.90	0.254	2.12
8.68	0.8850	10.20	13.07	0.277	2.11

21. Potassium Iodide.

13.37	1.0673	7.98	4.81	0.178	3.70
12.55	2.3096	18.40	11.08	0.491	4.23
11.37	4.9438	43.48	26.19	1.351	5.16

22. Potassium Iodide.

14.39	0.3113	2.16	1.30	0.038	2.92
13.08	0.8686	6.64	4.00	0.155	3.89
12.47	1.6945	13.59	8.19	0.315	3.85
11.81	3.1831	26.95	16.23	0.720	4.34

23. Potassium Iodide.

17.39	0.2934	1.60	1.04	0.016	1.59
16.08	0.9186	5.71	3.44	0.109	3.20
14.90	1.6414	11.01	6.64	0.248	3.78
13.75	1.8312	13.32	8.02	0.306	3.87

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
12.64	2.1414	16.94	10.20	0.408	4.05
11.99	2.1414	17.86	10.76	0.433	4.08
11.07	2.1414	19.34	11.65	0.471	4.09
10.44	2.1414	20.51	12.35	0.507	4.15
8.49	2.1414	25.22	15.80	0.650	4.33
18.87	2.1414	11.34	6.83	0.255	3.41
16.06	2.1414	13.34	8.04	0.306	3.85
14.43	2.1414	14.84	8.94	0.346	3.92
12.69	2.1414	16.87	10.16	0.412	4.10
12.04	2.1414	17.79	10.71	0.441	4.17
10.85	2.1414	19.74	11.90	0.480	4.09
10.31	2.1414	20.77	12.51	0.526	4.26
9.36	3.5356	37.77	22.75	1.129	5.02
8.52	4.4406	52.12	31.40	1.678	5.41
7.87	4.4406	56.43	34.00	1.994	5.94

24. Sodium Nitrate.

17.73	0.2744	1.53	1.80	0.043	2.37
16.63	0.2744	1.65	1.94	0.054	2.78
14.24	0.6066	4.26	5.01	0.150	2.99
12.94	1.2554	9.70	11.41	0.384	3.37
11.29	1.2554	11.12	13.08	0.457	3.49
10.41	1.7373	16.69	19.63	0.731	3.72
9.24	2.3107	25.01	29.42	1.190	4.04
8.30	2.7494	33.11	38.95	1.782	4.58
7.80	2.7494	35.24	41.46	1.997	4.82
6.65	2.7494	41.33	48.62	2.547	5.24

25. Ammonium Nitrate.

15.51	0.2924	1.88	2.35	0.087	3.69
14.46	0.2924	2.02	2.52	0.101	4.00
13.31	0.4920	3.70	4.62	0.166	3.59
12.38	0.7228	5.84	7.30	0.263	3.60
11.62	0.9776	8.41	10.51	0.388	3.69
10.73	1.2694	11.83	14.80	0.557	3.77
10.00	1.6499	16.50	20.62	0.834	4.03
9.42	2.0304	21.55	26.74	1.192	4.43
8.47	2.0304	23.96	29.94	1.368	4.57
7.32	2.0304	27.73	34.66	1.675	4.83
6.32	2.0304	32.12	40.15	2.100	5.23

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
		26. Metallic Sodium.			
10.20	0.1133	1.11	4.83	0.104	2.13
9.26	0.2145	2.31	10.04	0.207	2.07
8.43	0.3312	3.92	17.04	0.306	1.79
6.47	0.3312	5.10	22.17	0.317	1.43
		27. Metallic Sodium.			
14.10	0.1189	0.84	3.65	0.074	2.04
12.52	0.1189	0.95	4.13	0.090	2.18
10.82	0.1189	1.10	4.78	0.117	2.45
9.65	0.1189	1.22	5.30	0.134	2.53
8.51	0.1189	1.40	6.08	0.146	2.40
7.63	0.1189	1.56	6.78	0.159	2.35
		28. Metallic Sodium.			
16.87	0.6081	3.60	15.65	0.281	1.80
15.71	0.6081	3.87	16.83	0.296	1.76
14.09	0.6081	4.32	18.78	0.321	1.71
12.64	0.6081	4.81	20.92	0.335	1.60
11.04	0.6081	5.51	22.39	0.355	1.48
		29. Metallic Lithium.			
15.79	0.0580	0.36	5.14	0.040	0.76
13.76	0.1569	1.14	16.30	0.272	1.67
12.89	0.1569	1.22	17.43	0.293	1.69
10.18	0.1569	1.54	22.00	0.317	1.44
9.11	0.1569	1.72	24.60	0.335	1.36
8.25	0.1569	1.90	27.14	0.358	1.31
7.64	0.1569	2.05	29.30	0.390	1.33
6.84	0.1569	2.29	32.71	0.403	1.23
6.10	0.1569	2.57	36.71	0.446	1.22
5.46	0.1569	2.87	41.00	0.532	1.30
5.04	0.1569	3.11	44.43	0.600	1.35
4.84	0.1569	3.24	46.30	0.662	1.43

Summary of Results.

Water.—As the mean of two sets of concordant determinations, the constant of molecular elevation for water has been found to be 3.4.

Ethyl Alcohol.—The molecular elevation for ethyl alcohol is practically constant at 3.4 for all concentrations for which measurements have been made.

Propyl Alcohol.—For dilute solutions, 5 parts solute to 100 parts solvent, and under, the molecular elevation for propyl alcohol is practically identical with the constant for water and ethyl alcohol. With greater concentration the constant diminishes in value, reaching 2.75 for a solution containing 56.04 parts solute to 100 parts solvent.

Phenol.—In solutions of moderate concentration the molecular elevation of phenol is constant at about 3.0. With higher concentration the constant diminishes in value.

Pyrocatechin.—In solutions of moderate concentration pyrocatechin gives a molecular elevation of 3.2. With higher concentration the constant diminishes in value.

Resorcin.—The molecular elevation for resorcin is fairly constant for all concentrations for which measurements were made. The value of the constant is 3.5.

Hydroquinone.—Four sets of measurements were made on hydroquinone with not very satisfactory results. The mean values as calculated from the four sets of observations are, 3.8, 4.1, 3.5, and 3.7, respectively.

Sucrose.—Cane-sugar shows a fairly regular increase in the molecular elevation with rising concentration. Beginning with a value in the vicinity of 3.0 for the more dilute solutions, the molecular elevation increases in value until 4.7 is reached at a concentration of 75.79 parts solute per 100 parts solvent, the strongest solution measured.

Urea.—Beginning with a value approximately the same as that for water, the molecular elevation of urea diminishes with increasing concentration until a value of 2.26 is reached for a solution containing 26.53 parts solute to 100 parts solvent.

Pyridine.—In dilute solutions pyridine gives a molecular

elevation of about 3.2. With increasing concentration the molecular elevation was found to diminish in value. A solution containing 98.74 parts solute to 100 parts solvent, the strongest solution tested, gave an elevation of but 1.79.

Aniline.—The molecular elevation for aniline falls off somewhat with increasing concentration. The molecular elevation for dilute solutions seems to be greater than the constant for water. For the most concentrated solution upon which measurements were made, a solution containing 32.62 parts solute to 100 parts solvent, the molecular elevation was 3.12.

Acetic Acid.—Acetic acid reacts rather violently with ammonia, presumably forming ammonium acetate. The molecular elevation, however, which for moderate concentration was found to be about 2.0, decreasing to 1.58 for a solution containing 15.40 parts solute to 100 parts solvent, is calculated for acetic acid.

Orthonitrophenol.—Orthonitrophenol gives a molecular elevation distinctly larger than that given by phenol. The value is about 3.4.

Benzene.—For solutions of medium concentration, benzene produces a molecular elevation of about 2.5. In the more dilute solutions the elevation seems to be greater, reaching possibly a value above 3.0. Solutions of a concentration above about 12 parts solute to 100 parts solvent could not be tested because of the limited solubility of benzene in ammonia.

Salts.—Leaving out of consideration acetic acid and sodium acetate, we have so far measured the molecular elevation of but three salts, *viz.*, ammonium nitrate, sodium nitrate, and potassium iodide. Considering the fact that solutions of these salts in ammonia are good conductors of electricity, we expected to obtain values for the molecular elevation in the more dilute solutions very much higher than those actually measured. What may be the explanation of our apparently abnormal results; whether possibly the dissociation is really low, and the conductivity is made up by the higher velocity of a comparatively small number of ions, will have to be left

to the future to determine. Some experiments which show a rapid increase of the molecular conductivity of salt solutions with increasing dilution seem to indicate that possibly this explanation may be found to be the correct one. With the apparatus as used by us it is not possible to determine the molecular elevation of the boiling-point for very dilute solutions.

It seems reasonable to assume that the rapid rise of the molecular elevation with increasing concentration is due to the formation of a compound of ammonia with the salt.[1] It is interesting to note in this connection that if the solute, potassium iodide, be assumed to be in solution as $KI.7NH_3$, and the molecular elevation calculated in accordance with this assumption, then the values obtained for the successive measurements with the solution of potassium iodide, are respectively as follows: 1.59, 3.08, 3.49, 3.49, 3.56, 3.56, 3.53, 3.55, 3.55, 3.46, 3.49, 3.51, 3.61, 3.64, 4.51, 3.63, 3.67, 3.41, and 3.56.

Metallic Sodium and Metallic Lithium. — The very low molecular elevation for lithium and sodium, varying from 1.50 for the more concentrated solutions to about 2.30 for the more dilute, probably indicates the presence in solution of a molecule containing 2 atoms of the metal.[2]

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LXVII.—ON THE NON-EXISTENCE OF FOUR METHENYLPHENYLPARATOLYL AMIDINES.

[SECOND PAPER.]

BY H. L. WHEELER AND T. B. JOHNSON.

It might be expected that amidines containing two different radicals attached to the different nitrogen groups would exist in more than one form. For example, theoretically, two structurally different benzenylphenylparatolyl amidines might exist :

$$C_6H_5C\diagup^{NHC_6H_5}_{NC_7H_7} \quad \text{and} \quad C_6H_5C\diagup^{NC_6H_5}_{NHC_7H_7} \; .$$
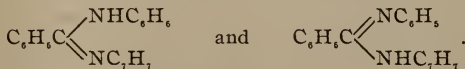
[1] Ostwald : Lehrb. d. allgemein. Chem., p. 473.
[2] Joannis : Compt. rend., **115**, 820 (1898).

These, since they contain the grouping $(R)R'C=N—R''$, might be obtained in the form of geometrical isomerides.

In the case just cited Pechmann[1] believed that he obtained two isomeric amidines, when, by the action of aniline on benzparatolylimide chloride, he obtained an amidine melting at 133°, while from benzphenylimide chloride and paratoluidine an amide melting at 128° was formed. These two products were so much alike in properties and behavior that only the difference in the melting-points prevented the recognition of their identity. This doubt, however, disappeared when Marckwald[2] showed that the melting-points are practically identical when the amidines are crystallized from absolute alcohol. Moreover, the chlorides and picrates agree in melting-points. Pechmann[3] then thoroughly examined a number of mixed amidines, prepared by methods which, if the reacting substances reacted by double decomposition, would have yielded isomers, but found that the resulting amidines were invariably obtained in only one form. Then followed the surprising result of R. Walther. He described the preparation of methenylphenylparatolyl amidine,

$$C_6H_5N=CH—NHC_7H_7 \quad \text{or} \quad C_6H_5NH—CH=NC_7H_7,$$
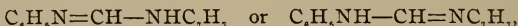
by four methods. Each method that he tried gave a new amidine, according to him, and these amidines were supposed to be isomers.

One of us was induced to examine Walther's products solely because his speculations, involving direct double decomposition, seemed incredible. The results obtained by crystallizing Walther's products have already been published.[4]

It was found that products melting near the temperatures given by Walther could be prepared, but these did not behave like pure substances, since on crystallizing a sufficient number of times the melting-points rose in each case. In one case (I. in table below) the melting-point finally coincided with that of methenyldiphenyl amidine. In another (II. in table below) with methenyldiparatolyl amidine. In the other

[1] Ber. d. chem. Ges., **27**, 1701.   [2] Ann. Chem. (Liebig), **286**, 348.

[3] Ber. d. chem. Ges., **28**, 869, 2363; *Ibid*, **30**, 1779 and 1783.

[4] This JOURNAL, **19**, 367.

two cases (III. and IV.) the melting-points became almost identical.

Since these results appeared Zwingenberger and Walther[1] have again published the original paper with the addition of a more detailed account for the preparation of the different products and have added along with other material the melting-points of the salts they examined.

In this last article they admit that one of their products (III.) passes into the other (IV.), "durch Erhitzen in Petroläther." In spite of this fact, previously shown by one of us (they ignore the results obtained by crystallization), Zwingenberger and Walther still maintain that these compounds are different amidines and that four methenylphenylparatolyl amidines exist. The method of preparation of these products, the salts and melting-points, as found by these authors, are given in the following table:

Results of Zwingenberger and Walther.

	Preparation.	M. P. of product.	M. P. of PtCl$_4$ precipitate.	M. P. of picrate.
I.	By fusing together methenyldiphenyl amidine and *p*-toluidine.	120°	213°	178°
II.	By warming in alcohol methenyldi-*p*-tolylamidine and C$_6$H$_5$NH$_2$.HCl	132°	127°[2]	209°
III.	From formtoluide, aniline and PCl$_5$.	98°	207°	196°
IV.	From formanilide, *p*-toluidine and PCl$_5$.	102°	218°	193°

From the work done by one of us we knew that Walther's products I. and II. contained unaltered methenyldiphenyl and methenyldi-*p*-tolyl amidines respectively. It only remained to mix with these amidines what one might expect to get, *i. e.*, either one of the products obtained in III. or IV., to solve the mystery of the four methenylphenylparatolyl amidines.

Product, M. P. 120°.—By mixing 8 parts methenyldiphenyl

[1] Jour. prakt. chem., **57**, 209.
[2] Probably misprint in Z. and W.'s article, and is intended for 217°.

amidine (m. p. 135°) with 5.5 parts of methenylphenylpara-
tolyl amidine (m. p. 98°–101°) and crystallizing this mixture
once from petroleum ether, a product identical in every re-
spect with the so-called methenylphenylparatolyl amidine of
Zwingenberger and Walther can be prepared. The melting-
point, behavior, appearance, all agree with the material pre-
pared according to their directions, and the salts obtained
from this mixture conform with surprising exactness with
those prepared by the methods of Zwingenberger and Wal-
ther. (See I*a* in table below.)

Product, M. P. 132°.—By mixing 3 parts methenyldipara-
tolyl amidine (m. p. 140°) with 1 part of methenylphenyl-
paratolyl amidine (m. p. 98°–101°), and crystallizing the mix-
ture once from petroleum ether the so-called methenylphenyl-
paratolyl amidine of Zwingenberger and Walther, melting at
about 132°, can be obtained. The close agreement of these
mixtures with the supposed amidines of Zwingenberger and
Walther is shown by comparing the following table with I.
and II. above:

Mixtures Prepared by Us.[1]

	M. P.	PtCl₄ pre-cipitate.	Picrate.
I*a*. 8 parts methenyldiphenyl amidine and 5.5 parts methenylphenylparatolyl amidine.	119°–124°	213°	177°–178°

[1] It is unnecessary to describe here the various mixtures or proportions we ex-
perimented with. Within fairly wide limits the same results are obtained, so that
the quantity of solvent is not given. A little more of the high-melting amidine raises
the melting-point of the mixture while more of the compound melting at 98°–101°
lowers the same. It is interesting to note that the lower-melting constituent that we
used melts lower than the mixture in both cases; no evidence of melting could be
detected in the mixture below the figures given, and, that while the product melting
at 98°–101° usually separates from ligroïn or petroleum ether in the form of needles,
nevertheless, when mixed with methenyldi-*p*-tolyl amidine, which separates in
prisms, only the prisms form, at least at first. A product prepared according to
Walther's fourth method, which usually forms prisms, melted at 105°. When mixed
with methenyldiphenyl amidine gave needles melting at 120°–125°. We now have the
explanation of Walther's results, in regard to the different crystalline forms of the
products melting at 98° and 102°. The material simply contains small quantities of
other amidines which not only affect the melting-point but determine what form
shall result, either needles or prisms.

We will further examine these points later in other cases. What seems to be the
best explanation of these curious facts is that the amidines form isomorphous mix-
tures, which, as experience teaches us, can only very slowly be separated by re-
peated crystallizations.

	M. P.	PtCl₄ precipitate.	Picrate.
II*a*. 3 parts methenyldi-*p*-tolyl amidine and 1 part methenylphenylparatolyl amidine.	131°–133°	216°	209°

From this it is conclusively proved that Walther's amidines melting at 120° and 132° are mixtures and are therefore to be stricken from the literature. Since the same methenylphenylparatolyl amidine can be used in both of the above mixtures it follows that *only one mixed amidine results when Walther's first and second methods are followed.* When, in the above mixtures, in place of the product melting from 98°–101° the material prepared according to Walther's fourth method is used, almost the same melting-points are obtained both in the case of the duplicated "amidines" and their salts. It follows, therefore, that *these products obtained by the third and fourth methods contain the same amidine. That there is therefore no proof of a direct double decomposition in these reactions, and that at the present time only one methenylphenylparatolyl amidine is known.*

In closing it may be stated that Walther determines structure by the method of preparation of amidines[1] in spite of the fact that Pechmann has shown, in numerous cases, that this is impossible. He states that from formanilide, paratoluidine, and phosphorus trichloride the following amidine must be formed, $C_6H_5NH—CH = NC_6H_4CH_3$. In other words, the action, according to him, must take place as follows:

$$HC \begin{cases} NHC_6H_5 \\ \boxed{OH_2} \, NC_6H_4CH_3 \end{cases} \quad \longrightarrow \quad HC \begin{cases} NHC_6H_5 \\ NC_6H_4CH_3 \end{cases}.$$
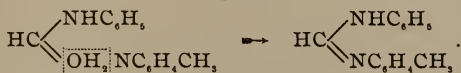
That the reaction does not proceed in this manner is shown by the fact that formanilide, methylaniline, and phosphorus trichloride give an excellent yield of methenylmethyldiphenyl amidine. Indeed, this appears to be a smoother reaction than when primary amines are used (see below):

$$HC \begin{cases} NHC_6H_5 \\ O + CH_3 \\ H \end{cases} > NC_6H_5 \quad \longrightarrow \quad HC \begin{cases} NC_6H_5 \\ N < \begin{smallmatrix} CH_3 \\ C_6H_5 \end{smallmatrix} \end{cases}.$$
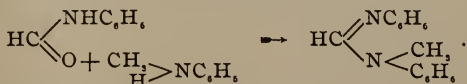
[1] Jour. prakt. Chem., **55**, 43 ; *Ibid*, **57**, 229.

In this case it is impossible for the reaction to proceed as Walther states.

This reaction in the case of primary amines is altogether too violent to be used to decide delicate cases of isomerism. Indeed it takes place with such energy that it has never happened in our work that the products obtained by one and the same method show even approximate agreement in their melting-points on crystallizing the same number of times. In one case in an attempt to prepare Walther's amidine melting at 98°, a product was obtained, which, after seven crystallizations from ligroïn, did not melt above 86°. In another attempt to prepare Walther's product melting at 102°, the only approximately pure product we could isolate was an amidine crystallizing in prisms like methenylphenylparatolyl amidine. This, however, did not melt at 102°, after five crystallizations, but from 134°–135°. If the compound had separated in the form of needles it would have been identified as methenyldiphenyl amidine; it was, however, probably methenyldiparatolyl amidine, but the quantity was too small to enable us to decide this point. Again, in one preparation of the compound melting at 102° a product was obtained that melted at 105°.

The conclusion from these results is that Walther's amidines said to melt at 98° and 102° (none of his amidines as obtained by us, melted sharply), undoubtedly contain more or less of these impurities which caused the observed variations in melting-points.

Eight years ago it was found by Comstock and Wheeler, although the results were not published, that phenylformimidomethyl ester and metanitraniline gave the same methenylphenylmetanitrophenyl amidine as metanitrophenylformimidomethyl ester and aniline. Since these reactions take place at ordinary temperature this method of studying possible isomers here is by far the best that has yet been employed. We propose to prepare methenylphenyl-*p*-tolyl amidine by similar methods and determine how far the pure product differs from Walther's compounds.[1]

[1] Since the above was written we have prepared this amidine by these methods and find that it melts at 86°, and also that all the products described by Walther as methenylphenyl-*p*-tolyl amidines are, without exception, mixtures.

Methenylmethylphenylamide-phenylimidine, $C_6H_5(CH_3)N$—
$CH=NC_6H_5$.—This amidine has been prepared now by
three methods.

I. It was first obtained by Comstock and Wheeler[1] by mix-
ing monomethylaniline with methylisoformanilide.

II. It has been obtained by us by adding a mixture of
monomethylaniline and formanilide, in molecular proportions,
to an excess of phosphorus trichloride. After the reaction
the excess of phosphorus trichloride was poured off and the
residue treated with pounded ice. On standing the material
dissolved, and to the cold solution cold sodium hydroxide was
added. This precipitated an amber-yellow oil, which was
extracted with ether and dried over calcium chloride. The
ether was then evaporated and the oil distilled at 25 mm.
pressure. It began to boil at about 95°, then the temperature
rapidly rose to 219°, when from 219°–220° all but a few drops
of material was collected. The first portion contained unal-
tered (?) material while the portion boiling between 219°–220°
consisted of almost pure amidine. From 10 grams of forman-
ilide, 4.5 grams of low-boiling, and 12.1 grams of material boil-
ing within one degree were obtained. The material thus ob-
tained had a slight odor of phenylisonitril. It was redistilled
at 30 mm. and again at 26 mm. pressure. That it was not
decomposed by this treatment is shown by the fact that it boiled
constantly at this pressure from 218°.5 to 219°. It still had
an odor of isonitril, but this was present only in very small
quantity.

III. In spite of the failures of Zwingenberger and Walther
to prepare this amidine from methenyldiphenyl amidine by the
action of methyl iodide, it can also be obtained in this way,
but the preparation by this method is not to be recommended,
as the yield, as determined by one experiment, is not good.
We observed its formation when 10 grams of methenyldi-
phenylamidine were heated with an excess of methyl iodide
to 135°–140° for seven hours. After evaporating off the ex-
cess of methyl iodide, a sticky colorless residue was obtained.
This was shaken thoroughly with ether and water. The

[1] This JOURNAL, **13**, 518; Beilstein [3], **2**, 346.

ether took up the color and the aqueous solution was only pale yellow. A solid residue remained that did not dissolve. This proved to be the hydrogen iodide salt of unaltered amidine. The aqueous solution was treated with cold sodium hydrate, and the resulting oil separated, dried, and distilled at 30 mm. pressure; 2 grams of colorless oil came over below 226°, mostly dimethylaniline, then 3.5 grams of material, the greater portion distilled constantly at 226°, while above this 1.3 grams of thick oil remained. The portion boiling at 226° was not pure, however; it had the odor of isonitril, and deposited on standing, or, when treated with ligroïn, crystals of unaltered methenyldiphenyl amidine. The ligroïn solution gave the salts described below.

Methenylmethylphenylamide-phenylimidine prepared by any of these three methods is a pale yellow, almost colorless, oil which in a freezing-mixture (—15°) gets thick and pasty but could not be solidified. It is readily soluble in cold petroleum ether and the ordinary solvents. When concentrated hydrochloric acid is added to the oil it gives the solid hydrochloride.

The Hydrochloride, $C_{14}H_{14}N_2HCl$.—This is best prepared by dissolving the amidine in petroleum ether and passing in dry hydrogen chloride. The precipitate crystallizes from absolute alcohol in large transparent colorless rhombohedrons or thick tables. It melts with decomposition at about 228°. A chlorine determination in the same prepared from the material obtained by the second method gave:

	Calculated for $C_{14}H_{14}N_2HCl$.	Found.
Cl	14.4	14.3

This salt is very soluble in water and decomposes on standing in alcoholic solution.

The gold chloride double salt, $C_{14}H_{14}N_2HCl.AuCl_3$, has well-characterized properties and easily serves to identify the amidine. It separates from alcohol by adding water in yellow, six-sided plates with growth markings parallel to the edges. Prepared from material obtained by any of the above methods it melted sharply at 145° (as previously described). A por-

tion made from material obtained by the second method above gave the following result :

	Calculated for $C_{14}H_{14}N_2HCl.AuCl_3$.	Found.
Au(196.7)	35.7	35.3

I.—AN ACTIVE PRINCIPLE IN MILLET HAY.

BY E. F. LADD.

As is well known among farmers, the exclusive feeding of millet (*Setaria Italica*) results in a diseased condition of horses which has come to be recognized as the " Millet Disease." One of the first symptoms is more frequent urination and an increased elimination. This feature is shown in case of the following animals—two horses. The daily average of urine for fourteen days when fed on hay was as follows :

	Urine per day. Grams.
Horse No. 1	7035.6
" " 2	5908.1

The same animals fed on millet gave the following daily average :

	Urine per day. Grams.
Horse No. 1	14404.9
" " 2	12258.0

The total solids in the urine averaged per day during the two periods :

	Hay fed. Grams.	Millet fed. Grams.
Horse No. 1	744.37	1127.9
" " 2	648.11	954.9

The urine contained of nitrogen on an average for the two periods :

	Hay fed. Grams.	Millet fed. Grams.
Horse No. 1	110.45	131.08
" " 2	90.39	121.35

These showed marked disturbance due to the action of some substance contained in the millet, and the continued use resulted in serious disturbances that have been described by Dr. Hinebauch.[1]

This work was undertaken to determine whether the millet hay contained an extractive principle capable of producing marked physiological disturbances, and to study the properties of the extract if such were found. For the present it became necessary to drop this work, and the results secured are herewith given with the expectation of investigating the subject more fully at some future time.

25 grams of the well-pulverized millet were treated in a separating-funnel for eight days with 250 cc. of petroleum ether. The product was then filtered and the filtrate evaporated to dryness. The total extractive residue amounted to 1.99 per cent. of the original millet.

The residue was then treated with 50 cc. of water slightly acidulated with sulphuric acid, for twenty-four hours, the filtrate was then transferred to a separating-funnel and agitated several times with ether to remove all fatty matter, and the aqueous solution preserved for testing.

The millet was again macerated for eight days in a separating-funnel with sulphuric ether, then filtered off, washed, and the extractive matter was found to be 0.86 per cent. of the millet. After treating the residue with 50 cc. of water slightly acidulated with sulphuric acid and allowing to stand for twenty-four hours, the aqueous extract was washed with ether and the water extract added to that previously secured from the petroleum extraction.

The millet was next macerated with alcohol for eight days and the extract evaporated to dryness over a water-bath. The total extractive matter was 6.53 per cent. of the millet. The ash was 0.28 per cent., leaving 6.25 per cent. of organic matter extracted by alcohol.

The extractive residue was then treated with 50 cc. of water and filtered off.

The extractive matter soluble in water taken out of millet

by the petroleum spirits and by the sulphuric ether gave no reactions for any unusual active principle, and our attention was then turned to the alcoholic extract.

Reactions of the Solution of the Alcoholic Extract.

The aqueous solution of the alcoholic extract treated with alkalies gave no reaction. Treated with warm nitric acid there was no reaction. With concentrated sulphuric acid the solution became brown in color. When treated with a solution of gelatin and plumbic acetate a yellow precipitate formed at once. Copper acetate gave no reaction, indicating the absence of tannins. The solution was quite bitter to the taste, and suggested the presence of some alkaloid or glucoside. The aqueous solution of the alcoholic extract was then made slightly acid with sulphuric acid, and agitated successively with petroleum spirits, benzene, and chloroform. After each successive agitation with the above menstrua, the solvent was separated and washed with pure water, the product evaporated to dryness, and the residue carefully examined for any active principle. The results are given as follows :

Extracts from the Acid Solution.

Petroleum Spirit Extract.—A small quantity of oily product remains on evaporating the petroleum spirits extract. (As a check the petroleum spirits on evaporation gave no residue.) This product had an acrid odor and taste and was insoluble in water. The amount was too small for other tests.

Benzine Extract.—On evaporating the benzine extract there remained an oily liquid of a light-yellow color, solidifying slightly below the ordinary temperature of the laboratory. It had a disagreeable, irritant odor, turned brownish on the addition of concentrated sulphuric acid, yellow with nitric acid, and gave a green precipitate with Frohde's reagent. Carbolic acid gave a reddish-brown color ; cane-sugar and sulphuric acid a violet color ; potassium nitrate and sulphuric acid a yellow color ; and with lead acetate a white precipitate was formed.

With the alkalies there was no reaction. When treated with acetyl chloride, the fumes being passed into a solution of argentic nitrate, a heavy precipitate was formed.

When treated with sulphuric acid the product was easily and quickly decomposed into a member of the glucose group capable of reducing copper from Fehling's solution.

Chloroform Extract.—A very small amount of material of a syrupy consistency remained on evaporating the chloroform extract. This product was nearly transparent, soluble in water, alcohol, and chloroform, but insoluble in petroleum spirits and benzine. On testing with hot dilute sulphuric acid it was converted into glucose. It is probable that this is a small portion of the same product as that described under the benzine extract, not fully removed by the treatment at that time.

A Glucoside.

The product extracted by benzine, as already described, is probably a glucoside. That it is not closely related to the tannins is shown by the negative reactions of the tests for tannins in the solution of the alcoholic residue before the separations were made. It has a bitter acrid taste and a pungent odor.

Of the glucosides with which I am familiar it most resembles daphnin, $C_{31}H_{34}O_{19}$, which is somewhat soluble in cold water, alcohol, and benzine, but insoluble in petroleum spirits. Daphnin is precipitated by plumbic acetate; acids resolve it into glucose, and alkalies color it yellow. In this last respect as well as in some others it differs wholly from the product we are dealing with. Daphnin is a bitter glucoside having a marked influence on the secretions, especially those of the skin and kidneys. Daphnin also forms colorless rectangular prisms when its aqueous solution is evaporated. The glucoside from millet hay forms no crystals when its water solution is evaporated, but an amorphous mass is left behind. That it is possessed of active physiological properties is indicated by experiments already mentioned, and that the product we have extracted and examined possesses this principle in a marked degree is shown by some experiments made by Mr. C. G. Warner, then a special student in my laboratory.

Physiological Action.

Some of the extract was prepared as indicated above, and the benzine extract, after separating it, as far as seemed possible, from other products, was then evaporated to dryness and again brought into solution with distilled water, and a series of experiments made upon mice, rats, and young cats to learn something of the effects of administering these products. To each of the animals were fed small quantities of the aqueous extract mixed with their food. In about two hours after feeding the reactions in each case were very marked upon all the animals under experiment. Urination was very frequent, every fifteen to twenty minutes, for some time, and the animals were stupefied as though from the action of some strong toxic product. The animals would stand upon their hind feet, their front feet stretched out before them, resting their nose upon the bottom of their pens, and, when forced to move about, they did so reluctantly and with a very unsteady gait, especially in their fore quarters. Of their hind legs they seemed to have pretty full use.

Hypodermic injections of the aqueous solution acted in the same manner, but more rapidly than when the extractive matter was administered with the food. Characteristic crystals were also formed with platinic chloride.

At this point Mr. Warner could no longer continue the work, and nothing more has since been done in this line.

Extracts from the Alkaline Solution.

The aqueous solution of the alcoholic extract, from which the acid extract (see above) had been prepared, was then made slightly alkaline and the agitation repeated as with the acid solution, petroleum spirits, benzine, and chloroform being used.

Nothing was separated or extracted by petroleum spirits or chloroform.

Benzine Extract.—A light-yellow, oily, and bitter liquid was removed by benzine from the alkaline solution. This product did not yield glucose by the action of sulphuric acid. The following color reactions were secured : Treated with

sulphuric acid it became dark-brown, gradually becoming lighter in color with the formation of a small precipitate. Frohde's reagent gave a dark-green color, sulphuric acid and cane-sugar gave a violet color, and with sulphuric acid and potassium bichromate it gave a peacock-blue color.   Hydro-chloric acid, nitric acid, ferric chloride, and sulphuric and nitric acids gave no reactions.   It hardly seems probable that this product could be an alkaloid.   It certainly is not a glu-coside.   Its physiological action was not studied, and lack of material prevented further tests at the time.   At some future time it is proposed to continue this work, to prepare and purify the product, and to determine the composition and for-mula of the glucoside.

Much of the analytical work in the foregoing investigation was done by Mr. R. D. Ward, assisted by others who have been students in my laboratory.

II.—COMPARISON OF METHODS FOR ESTIMATING CAFFEÏN.

BY E. F. LADD.

In making estimations of caffeïn it was necessary to make some comparative determinations of the value of different methods for the estimation of caffeïn in tea.   Four methods were tried, Vite's, Peligot's, Crosschoff's, and Gomberg's. Briefly, the methods employed by us were as follows :

Vite's Method.—Five grams of the tea or other product, finely pulverized and extracted with 100 cc. of water, are kept at boiling for one hour, and then the solution decanted off. This extraction was repeated three times, and the combined filtrates concentrated on the water-bath to 75 cc. and mixed with freshly precipitated lead oxide and sand.   The mixture is dried on a water-bath, powdered, and boiled with chloro-form for three hours.   The chloroform solution is then fil-tered off, evaporated to dryness, and the residue taken up in hot water.   The clear aqueous solution is evaporated on the water-bath, dried at 100° C., and weighed.

Working on pure caffeïn by this method there was a loss of 10 per cent., and when working with tea in comparison with the other methods the loss was as much as 42 per cent. It seems that the caffeotannate is not wholly broken up by the lead oxide when working with samples of tea or coffee, and no further attempts were made to use this method.

Gomberg's Method.—The solutions necessary for this method are :

A solution of potassium iodide made by dissolving 18 grams of the pure salt and 12.65 grams of iodine in 250 cc. of water, and when dissolved diluting with distilled water to 1000 cc.

A solution of sodium thiosulphate made by dissolving 24.8 grams of the crystallized salt $Na_2SO_3.5H_2O$, in 1 liter of water. This solution is then standardized by means of a standard solution of potassium chromate, made by dissolving 4.913 grams in 1 liter of water. After the solution of the thiosulphate has been properly standardized by means of the solution of chromate, the solution of the iodide may be standardized by means of the standard sodium thiosulphate. The solution should then be kept in the dark.

The method, as employed, consists in boiling a definite quantity of tea, coffee, or other product with water, making up to a known volume, and then filtering. An aliquot portion is then treated with basic lead acetate as long as a precipitate is formed. After standing to allow the precipitate to settle, it is filtered off and the filtrate carefully treated with hydrogen sulphide to remove the excess of lead which is then filtered off. The filtrate is then boiled to drive off the excess of hydrogen sulphide and divided into two equal portions. One portion is acidified with sulphuric or hydrochloric acid, and each is then treated with a definite quantity of the standard solution of iodine. After allowing to settle for five or ten minutes it is filtered, and the filtrate treated with the standard tenth-normal solution of sodium thiosulphate.

The first solution without acid serves to show whether there is any product present that can be precipitated by Wagner's reagent. Should there be any, a corresponding correction will be necessary. One cc. of the sodium thiosulphate corresponds to 0.00485 gram of caffeïn.

By this method, working with o.1 gram and o.2 gram of pure caffeïn, 99.9 and 100.5 per cent., respectively, of caffeïn were removed, showing most excellent results ; and, when working on teas, higher and apparently more nearly accurate results were obtained than by either of the other methods.

Peligot's Method.—Ten grams of tea were weighed out and 250 cc. of water at 100° C., added and allowed to stand for fifteen minutes. This is then filtered through a fine cloth and a solution of basic lead acetate added to precipitate all the tannin, the precipitate allowed to settle, and then filtered. The filtrate is then treated with hydrogen sulphide to remove all excess of lead. The solution is then filtered off, the filtrate evaporated to dryness, and weighed. An excess of lead and prolonged treatment with hydrogen sulphide results in diminished amount of caffeïn, possibly from the action of the sulphide on the caffeïn. Working with pure caffeïn the results agree closely with those obtained by Gomberg's method.

Crosschoff's Method.—A decoction is made with 1 ounce of tea and 600 to 1000 cc. of cold water. The temperature is then gradually raised to boiling, and the solution allowed to stand for a few minutes, when it is filtered through a cloth. About 3 grams lead oxide is added to the filtrate, and it is made alkaline by the addition of potassium chlorate. This is allowed to stand for a few hours, and then it is evaporated to a syrup. The caffeïn is dissolved out with about 400 cc. of alcohol, the solution filtered, the alcohol evaporated off, and the caffeïn allowed to crystallize. The crystals are redissolved in alcohol, the solution passed through a charcoal filter, and evaporated to crystallization. The residue is then dried and weighed.

With pure caffeïn good results were obtained by this method. The following table gives results secured with three samples of tea by these methods :

Per Cent. of Caffeïn Found.

Method.	Congo.	Green tea.	Gunpowder.
Peligot	0.843	2.061	3.680
Crosschoff	0.919	2.031	3.200
Gomberg	1.542	2.386	3.986

It will be seen that higher results were uniformly secured working with Gomberg's method than by either of the others and its simplicity makes it the most desirable method for rapid work where caffeïn has to be determined.

The analytical work has all been performed by Mr. Benn, a senior student in my laboratory.

AGRICULTURAL COLLEGE, N. D.,
    July 29, 1898.

III.—CREATIN AND ITS SEPARATION.

BY E. F. LADD AND P. B. BOTTENFIELD.

In some work on the alloxuric bodies resulting from metabolism undertaken by one of us (E. F. L.), it was found desirable to make some investigation relating to creatin and to be able to determine and identify it. For that purpose a comparison of the principal methods employed in its determination was undertaken, and the final results as secured by one of us (P. B. B.) are here presented for the purpose of showing the value of the methods for the conditions under which we were obliged to work. The three methods employed were Neubauer's, Liebig's, and Stradeler's, the determinations being made as follows :

Neubauer's Method.—The meat is first cut into very small pieces by running it through a sausage machine. 700 grams of this product were then extracted for ten to fifteen minutes with an equal weight of water at 55°–60° C. It is then pressed with a screw-press and again extracted as before with water. The two extracts united are then heated to boiling to coagulate the albumin. After filtering, the filtrate is treated with basic lead acetate as long as a precipitate forms ; the excess of lead is then removed from the filtrate by hydrogen sulphide. The filtrate is now carefully concentrated to a small volume on the water-bath, and then allowed to stand for several days to allow the creatin to crystallize. The crystals of creatin are now collected on a filter-paper and well washed with alcohol. The crystals thus secured are redissolved, filtered through charcoal, and again recrystallized, well washed with alcohol, dried, and weighed.

Liebig's Method.—The product is reduced to a fine state of division, in case of meat, by passing through a sausage machine, and then extracted with one-half its weight of cold water for a few hours, then pressed with a screw-press, and again extracted in the same manner with cold water. The two filtrates united are heated to boiling to coagulate the albumin, and to the filtrate baryta water is added to remove the phosphates. The excess of barium is then removed by carbon dioxide. After filtering and washing, the filtrate is evaporated on a water-bath to a syrupy consistency, and then allowed to stand for several days so that all the creatin may crystallize out. The crystals are then removed, washed with alcohol, and purified as in Neubauer's method.

Stradeler's Method.—The finely divided material is digested on the water-bath with twice its volume of alcohol for several hours, then pressed as in the preceding methods. The filtrate is evaporated to a small volume. A solution of basic lead acetate is then added as long as a precipitate is formed, and the process continued as in Neubauer's method.

Samples of flesh from an ox and from a dog were treated by these three methods with results as presented below :

Per Cent. of Creatin.

	Neubauer's.	Stradeler's.	Liebig's.
Ox	0.250	0.234	0.215
Dog	0.242	0.230	0.218

Voit in his experiments found in the flesh of the ox from 0.219 to 0.276 per cent. of creatin, and in the flesh of the dog the same investigator found from 0.223 to 0.248 per cent.

It will be seen that the above results are in accord with those found by Voit for the same animals. The method of Neubauer gives results somewhat higher than those by the method of Stradeler or that of Liebig.

In Liebig's method there are several sources of error. The use of cold water does not leave the meat in as good condition as in Neubauer's method, and it is impossible to press the meat as dry. Again we were not able to remove all traces of the barium by means of carbon dioxide without some loss of creatin. The use of alcohol in Stradeler's method results in extracting some of the fats and other products, and a re-

moval of these products results in some loss of creatin, but this is not as great as in Liebig's method.

AGRICULTURAL COLLEGE, N. D.,
August 7, 1898.

A DOUBLE CITRATE OF ZIRCONIUM AND AMMO-NIUM.

By S. H. Harris.

The chlorides of zirconium used were those obtained by dissolving zirconium hydroxide, $Zr(OH)_4$, in concentrated hydrochloric acid, and repeatedly crystallizing from the same. The mixed chlorides were then recrystallized from water. A portion of the mixed chlorides was dissolved in eight to ten times as much water. To this was added an aqueous solution of ammonium citrate (1–5) drop by drop, with constant stirring, until the precipitate ceased to form. The precipitate comes down as a white, curdy mass, and is very easily soluble in even a slight excess, so that great care must be exercised. When the maximum amount of precipitation had occurred, hot water was added and the mass filtered off on a large plain filter. The precipitate was then washed back into the beaker with hot water, well stirred up and filtered again. After two or three more such washings the filter-paper containing the precipitate was spread open to dry on an unglazed porcelain plate. When dry it was pulverized, placed on a watch-glass, and heated to 100° C. in an air-bath for several hours. The substance proved to be very deliquescent; so much so that it could not be weighed in an open glass. It was then placed in a weighing-bottle and heated in an air-bath at 100° C. for six hours, the stopper replaced quickly, and weighed. During the intervals between the heatings the weighing-bottle containing the double salt was kept in a desiccator over concentrated sulphuric acid.

No. of heating.	Hours.	Temperature.	Wt. bottle + citrate. Grams.	Moisture driven off. Gram.
1	6	100°	24.5916	....
2	6	110°	24.5211	0.0705
3	6	120°	24.4465	0.0746
4	6	120°	24.4151	0.0314
5	6	120°	24.4108	0.0053
6	6	120°	24.4108	0.0000

Here the heating was stopped, as the substance lost no more water, and seemed to have come to a constant weight. A small portion of the substance was ignited in a platinum crucible. It chars at first, showing the presence of citric acid, and on complete ignition leaves a white residue of zirconium oxide, ZrO_2. The ammonia is held very firmly in combination, and can only be driven off by boiling with a solution of sodium hydroxide.

Estimation of Zirconium.—The double citrate, after the drying previously described, was poured out of the previously weighed weighing-bottle into a large platinum crucible, as quickly as possible, the stopper replaced, and the bottle weighed again. The crucible was then heated on a sand-bath until it had charred and the combustion slowly and cautiously completed with a Bunsen burner until the residue of zirconium oxide was perfectly white. For this analysis 0.626 gram of the citrate was taken. I found $ZrO_2 = 0.3593$ gram, which, taking the atomic weight of $Zr = 90.6$, gives 0.2655 gram Zr, or 42.40 per cent. Zr.

Attempt to Estimate Citric Acid.—For this analysis 1.9705 grams were taken. An attempt was made to dissolve this in dilute sulphuric acid (1–20), but the citrate was only very slightly attacked, even when the acid was heated to boiling. The liquid was filtered off, however, from the unchanged citrate and titrated in a porcelain dish at 60°–70° C., against a standard solution of potassium permanganate, but only 14 cc. were necessary, showing that very little of the citrate had been attacked. It is impossible to get the substance to dissolve without decomposition, and hence the citric acid determination had to be abandoned. This being the only available method with this particular substance, it was impossible to determine the citric acid.

Estimation of Ammonia.—A portion of the citrate was analyzed by the Kjeldahl method for ammonia and 11.92 per cent. found. The formula $Zr_2(C_6H_5O_7)(NH_4)_3$ agrees fairly well with the results obtained for zirconium and ammonia.

	Calculated.	Found.
Zr	42.71	42.40
NH_3	12.02	11.92

NOTE.

Xenon, Etherion, and Monium.

In a note in a recent number[1] of this JOURNAL the methods used by Ramsay for the isolation of krypton, neon, and metargon were described. Since the publication of that paper another gas has been added to the number of those obtained from the liquefied argon. This gas, to which the name "xenon" has been given, can be readily separated from the others as it has a higher boiling-point and remains behind after the others have evaporated. Its spectrum is analogous to that of argon; but the lines occupy a different position in the spectrum and the colors vary according to the methods used to produce the discharge. All these gases exist only in minute quantities, the amount of neon being about 1 part to 40,000 of air.

At the summer meeting of the American Association for the Advancement of Science a paper entitled "A New Gas" was read by Mr. Chas. F. Brush. During an investigation of the heat conductivity of gases at different pressures the author found that a substance could be extracted, at low pressures, from glass, and that the behavior of the substance thus extracted was entirely different from that of all known gases. By heating pulverized glass he obtained a gas which had a heat conductivity, at a pressure of 0.12 of a millionth, forty-two times that of hydrogen. This gas, which is present in the air, is absorbed by many substances; but especially by glass, and the supply of the gas in the glass can be renewed by exposing the glass to the air. He can separate the gas from other substances, to a considerable extent, by diffusion through a porous porcelain tube, and he considers from the results already obtained, the value 100 as a fair one for the relative heat conductivity of the pure gas, if hydrogen = 1. From this the molecular velocity was calculated and the result showed a velocity of 105 miles per second. On the basis of this the density would be 0.0001 if H = 1, and the molecular weight would be 0.0002. The great velocity would make it impossible for this gas to remain in the atmosphere unless the space above also contained it. The author suggests that perhaps this is the ether of the physicist to which such remarkable properties have been ascribed, and he suggests the name "etherion" for it.

In *The Chemical News* of Nov. 4, 1898, there is an article by Sir William Crookes in which he describes some experiments that lead him to "consider it more probable that etherion is water vapour than that it is a new elementary gas."

Sir William Crookes, who has been working for a number of

[1] This JOURNAL, **20**, 696.

years on the separation of the constituents of yttria, has iso-
lated a new elementary substance from this material. By
skilful methods of fractionation, using a specially designed
form of the spectroscope to test the relative amounts of the
substances present, he has isolated a substance which gives a
characteristic series of lines at the extreme end of the ultra-
violet spectrum. He has given it the name '' Monium'' from
the Greek word for '' alone.'' This substance, unlike the
gases discovered by Ramsay, readily forms compounds with
other elements, and although the details of the investigation
have not yet been published, the author states that the atomic
weight will be very close to 118.   J. E. G.

REVIEWS.

LEHRBUCH DER ANORGANISCHEN CHEMIE. By DR. HUGO ERDMANN,
Professor in the University of Halle. Braunschweig: F. Vieweg
und Sohn. 1898. pp. xxvi, 756.

Any one who is familiar with Professor Erdmann's use-
ful little book on the preparation of inorganic compounds will
at once welcome the idea of a larger work from the same pen.
It is a pleasure to say that this new volume will not disap-
point such expectations. Considering its size, the book is an
unusually comprehensive treatise upon the experimental side
of modern inorganic chemistry, and the reader is attracted by
the scope of the writer's knowledge, as well as by his ability
in compressing this knowledge into clear, concise, readable
language. Some text-books endeavor to express a great deal
in a few pages by systems of abbreviation, but Professor
Erdmann has avoided this unfortunate method. He has
adopted two sizes of type, and a system of useful marginal
references, which enable one to read in an uninterrupted
manner either the salient features, or the less important de-
tails, or both, as the reader may wish ; and has illustrated his
book by an unusually large number of good wood-cuts and
three remarkably brilliant plates of spectra. The arrange-
ment is, of course, based primarily on the periodic system, after
an introduction containing an essay on measurement, num-
ber, and the general principles of physics which underlie chem-
ical phenomena. One is rather surprised to find the descrip-
tion of the periodic system itself at the very end, where also are
to be found the scanty pages devoted to the hypothesis of
electrolytic dissociation. In view of this latter circumstance,
one cannot but regret that more ancient theories have been
treated almost as facts ; indeed the book is hopelessly old-
fashioned on the theoretical side. Since, however, it does not
pretend to be a treatise on theoretical chemistry, the lack of

prominence given to modern generalizations may perhaps be pardoned, and one should turn rather to the treatment of the facts. Here especial emphasis is laid upon recent discoveries, and upon all those chemical relations which are most intimately connected with the life of man. The organisms of nitrification, argon, helium, liquid air, fluorine, the electric furnace and the carbides, as well as the Welsbach light, all receive satisfactory treatment; and the historical, economic, and toxicological details throughout are apropos and interesting. Even krypton, neon, and metargon find a place in a note at the conclusion.

Of course, an occasional inaccuracy in such a work is inevitable, but one regrets to find the book marred by a large number of mistakes. The change from an old standard of reference to a new one is a process fraught with possibilities of error, and Professor Erdmann, in the premature use of hydrogen instead of oxygen as a standard of atomic weights, has not escaped an occasional lapse. One is not much surprised, for example, to find that the specific gravity of air referred to hydrogen is given at 14.44. More surprising is his history of the discovery of helium, in which the name of Ramsay does not appear; that of nitrogen chloride, from which Gattermann's name is omitted; and that of the atomic weight of oxygen, where the value 15.88 is ascribed to Keiser, without mention of the name of Morley. Distilled dilute nitric acid should certainly not be called $N(OH)_5$ because it happens to contain about 36 per cent. of water. In the explanation of the economy of the atmosphere, the fact that the absorption of carbon dioxide by plants is a process of assimilation and not of respiration, and that most plants, in common with other organisms, require oxygen to sustain life, is not made clear. The table of magnitudes given at the end, while compassing the distances of the fixed stars as well as the size of the hydrogen atom, is not adapted to assist the average imagination in either direction. But in spite of these and other deficiencies, the book is so full of admirable material that it will undoubtedly serve a very useful purpose, especially as an experimental guide to the teacher of the facts of inorganic chemistry.

T. W. R.

INORGANIC CHEMISTRY ACCORDING TO THE PERIODIC LAW. By F. P. VENABLE, University of North Carolina, and JAS. LEWIS HOWE, Washington and Lee University. Easton, Pa.: The Chemical Publishing Company. 1898. pp. 266. Price, $1.50.

In preparing their book the authors have followed the advice given by Lothar Meyer in his lecture before the German Chemical Society, and "have made the experiment of a com-

plete and faithful introduction'' of the system recommended by him. They say : "In no other way have we been able to secure such excellent results both as to thorough systematic instruction and economy of time.'' The matter is presented in the order below indicated :

PART I.—Introduction ; Definitions ; Nomenclature ; System ; Laws.

PART II.—The Elements : Their History, Occurrence, Preparation, Properties.

PART III.—The Compounds of the Elements with Hydrogen, or Hydrids.

PART IV.—The Compounds of the Elements with the Halogens, or Halids.

PART V.—The Compounds of the Elements with Oxygen, or Oxids ; the Compounds with Sulphur, or Sulphids ; Selenium ; Tellurids.

PART VI.—The Nitrids, Phosphids, Carbids, Silicids, and the Alloys.

At the end of PART I we find this paragraph : '' This introduction contains, in outline, some of the great principles of the science. It is scarcely expected that they will be fully grasped and comprehended by the student just entering upon the study. He is rather to look upon much of it as a statement of what is to be proved by his further study. A good deal will be repeated in suitable places later when the facts have been acquired which will render explanation possible. It is scarcely practicable to start upon the study of the science without some such frame-work for the building.''

If instead of saying '' it is scarcely expected that they will be fully grasped and comprehended by the student just entering upon the study'' the authors had used the stronger expression : "It is certain that the student just entering upon the study will not comprehend what has gone before," they would have stated what every experienced teacher knows to be true. A college president once said to a teacher of biology : '' I suppose you will begin your course by a statement of the general principles of the science.'' The teacher answered : '' No, I shall begin with a bushel of clams.'' That teacher had been trained by Agassiz, and knew how to teach.

It is impossible to judge of the merits of a method of presentation without trying it, and the writer of this notice, while admitting that the plan suggested by Lothar Meyer and followed by the authors of this book does not commend itself to him, is willing to admit that his judgment may be at fault. Let those who feel otherwise try the book and judge it by the results.

As far as the contents of the book are concerned, leaving out of consideration the plan, it need hardly be said that they give evidence of scholarship on the part of the authors, and that there is much in the book that merits commendation.

I. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS (Braunschweig), C. A. BISCHOFF (Riga), E. F. DÜRRÉ (Aachen), J. M. EDER (Wien), R. FRIEDLÄNDER (Wien), C. HÄUSS-ERMANN (Stuttgart), F. W. KÜSTER (Göttingen), J. LEWKOWITSCH (Manchester), M. MÄRCKER (Halle), F. RÖHMANN (Breslau), K. SEUBERT (Hannover), herausgegeben von RICHARD MEYER (Braunschweig). VII Jahrgang. 1897. Braunschweig: Druck und Verlag von Friederich Vieweg und Sohn. 1898.

Attention has been called to this excellent publication year after year since the appearance of the first volume in 1891. Here is the seventh volume. "Good wine needs no bush;" and this is in fact "good wine." Even the best-read chemist will find the book profitable. If he will from time to time during the year "finger the pages" he will be sure to be rewarded by finding clear and concise reports of articles which he may have read at the time of their publication, and also of some that may have escaped his serious attention. It is a good book to have at hand for frequent reference, even though one has also the more elaborate *Centralblatt*. I. R.

TEXT-BOOK OF MEDICAL AND PHARMACEUTICAL CHEMISTRY. By ELIAS H. BARTLEY, B.S., M.D., PH.G., Professor of Chemistry and Toxicology in Long Island College Hospital, etc. Fifth edition. Revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1898. 738 pp. Price, $3.00.

That medical students ought to know something about chemistry no one will deny. That they are not likely to learn much about it after entering the medical school most will admit. The conditions are there unfavorable, and necessarily so, for the study of any one of the fundamental sciences. The students are interested in matters that pertain directly to the practical side of medicine, and have no time to dwell upon chemical phenomena as such to a sufficient extent to reach a comprehension of the simplest of these. It would be best for them to get their chemistry before going to the medical school and, as is well known, efforts are being made in various places to secure this. But here again, how much chemistry can one acquire in a year's course even under the best of circumstances? Let those who have tried the experiment make answer.

All this is suggested by the book of the above title. As long as the present conditions continue, it will probably be neces-

sary to have books of this kind that give a little physics, more chemistry, and considerable pharmacy, with a touch of physiology. One cannot help pitying the student who is expected to master the contents of the book. If he should succeed he would have "all the chemistry that every educated doctor ought to know" and a great deal more. He would be especially qualified to revel in constitutional formulas. To be sure, he might find it difficult to tell what they mean, but this is true of some chemists. A great and good bishop once said to the writer : " I imagine any man would be much surprised if he could learn just what idea of God is entertained by his neighbor." Surprise would probably give way to utter astonishment if one could learn what idea of pinene, terpinin, terpin, and terpin hydrate is entertained by the student who has studied page 324 of this book. In introducing the benzene series the author says : " The compounds of this series differ from all others thus far mentioned in the structure of their molecules in that the carbon atoms are arranged in the form of a closed chain, or cycle, at the angles of a regular hexagon." That statement is definite enough. The carbon atoms are at the angles of a regular hexagon. What idea does that convey to the medical student? The plot thickens as we advance. If there is one substance above another that it behooves a medical student to study, it is albumin. By the time he reaches page 515 he will be pleased to learn about the hemi-group and the anti-group ; the hemi-proto and the anti-proto ; hemi-deutero and the anti-deutero albumoses. And so on to the end.

In general, the presentation is clear, but it appears to the writer that the author has attempted too much if this book is intended for medical students. It may serve a useful purpose as a book of reference for the practitioner. But there is much in the purely scientific parts that needs modification.

I. R.

SOAPS. A practical manual of the manufacture of domestic, toilet and other soaps. BY GEORGE H. HURST, F.C.S. London: Scott, Greenwood, & Co., and New York : D. Van Nostrand Company. 385 pp. Price, $5.00.

In his preface the author says : " The substance of this book has already appeared in the form of articles in the pages of the *Oil and Colourman's Journal.* These articles were received with so much favor by the readers of that Journal that it has been thought desirable to collect them together and reprint them in book form. For this purpose the articles have been thoroughly revised and new matter added to bring the subject up to date. The author has not attempted to write a

complete treatise on soap manufacture, but has aimed at presenting in a brief but, it is hoped, clear manner the principal processes of soap manufacture, with an account of the raw materials used and the scientific principles which underlie the various operations.''

The book is made up of ten chapters in which the following subjects are presented : I. *Introductory :* Soap, Nature of Soap, Action of Soap ; II. *Soap-makers' Alkalies* ; III. *Soap Fats and Oils ;* IV. *Perfumes ;* V. *Water as a Soap Material ;* VI. *Soap Machinery ;* VII. *Technology of Soap-making ;* VIII. *Glycerine in Soap Lyes ;* IX. *Laying Out of a Soap Factory ;* X. *Soap Analysis.* The treatment is clear and the book carries upon its surface the evidence that the writer knows his subject. The important experiments of F. Krafft on the action of soap seem to have escaped the notice of the author.

MANUAL OF DETERMINATIVE MINERALOGY WITH AN INTRODUCTION ON BLOWPIPE ANALYSIS. By GEORGE J. BRUSH, Revised and enlarged, with entirely new tables for the identification of minerals by SAMUEL L. PENFIELD. Fifteenth edition. New York : John Wiley & Sons. 1898. 312 pp. 8vo. Price, $3.50.

The appearance of this book marks the completion of a revision of this well-known and highly valued text-book which first appeared in 1874. Although the work was reached its fifteenth edition, few changes were made in text or tables until 1896. At this time the first 150 pages appeared in a rewritten and enlarged form that increased the value of the book by the introduction of new tests of decisive and practical character—by the simplification of previous methods and by the addition of many helpful suggestions based on Professor Penfield's experience as a teacher and as an investigator. The new analysis of the presentation and the revised phraseology in the descriptions of methods and apparatus also add much to the clearness of the treatment.

The edition which has just been issued removes one of the two glaring defects in the preceding issue. The tables are revised but the same lack of finish in the art of book-making remains. It seems a shame that text of such high order should be presented to the reader on such poor paper and accompanied by such imperfect figures. Neither of the latter is at all in keeping with the price of the book or the usage to which it must be subjected.

Two features are of especial value in the present editions— the added chapter on the physical properties of minerals and the revised tables. In the first the crystallographic treatment is marked by the acceptance of the recent classification of

forms into thirty-two classes and the rejection of all systems of notation except that of indices. Although certain of the classes are omitted the general discussion is characterized by its balance and its concise, clear descriptions of those mentioned. This chapter will prove valuable to chemists and mineralogists who desire a short presentation of crystal symmetry from the point of view which is accepted at the present time. It also offers succinct descriptions of the methods of determining the specific gravity and the purity of mineral fragments by means of heavy solutions.

The determinative tables are newly prepared on the same general plan as that employed in previous editions and are brought up to date by the insertion of many new minerals and more approved and more distinctive tests for previously recognized species. The total number of minerals included reaches full 800 and the relative importance is indicated by differences in the type. E. B. MATHEWS.

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